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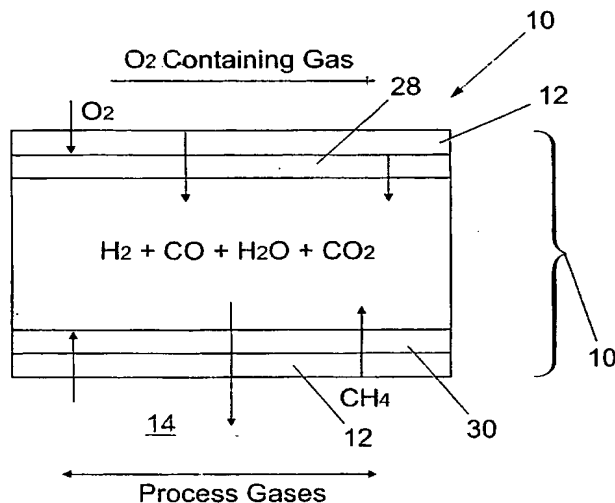
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(54) Title: A MEMBRANE APPARATUS AND METHOD OF PREPARING A MEMBRANE AND A METHOD OF PRODUCING HYDROGEN



(57) Abstract: The present invention discloses a method, apparatus and method of manufacturing an apparatus; all to produce hydrogen gas, particularly synthesis gas. Preferred embodiments of the invention include an alpha alumina membrane which has been treated with a TiO<sub>2</sub> wash coat on one side and has an active gamma alumina layer on an opposite side. A metal catalyst, preferably rhodium, is deposited within the pores of the alumina. Oxygen travels through the membrane and is activated before contacting methane on the other side of the membrane and forming synthesis gas through partial oxidation of the methane. Embodiments of the invention have a number of benefits including the high conversion rate of oxygen (100 %), the separate feed streams of methane and oxygen which allow for optimal ratios to be used without danger of explosion, and the opportunity to vary the feed rates without changing the products

formed. Normally gaseous hydrocarbons recovered from remote oil wells (e.g. offshore oil wells) can thus be converted to synthesis gas and then to normally liquid hydrocarbons via a Fischer-Tropsch type reaction. The normally liquid hydrocarbons are easier to transport away from the remote oil well than normally gaseous hydrocarbons.

WO 2004/098750 A1



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1     A Membrane Apparatus and Method of Preparing a  
2     Membrane and a Method of Producing Hydrogen

3  
4     The present invention relates to a membrane and a  
5     method of preparing the membrane, the membrane being  
6     particularly, but not exclusively, useful in  
7     producing synthetic gas for use in Fischer-Tropsch  
8     gas-to-liquids production in the oil and gas  
9     exploration industry or for producing hydrogen for  
10    use as a fuel.

11  
12    While offshore oil production has risen slightly in  
13    recent years, natural gas (which mainly consists of  
14    methane) production has seen a marked increase.  
15    Natural gas is often extracted during the extraction  
16    of liquid hydrocarbons, such as oil, from the ground  
17    and is often undesirable due to the lack of  
18    infrastructure to transport the natural gas to an  
19    onshore location. The lack of infrastructure can be  
20    explained by the physical nature of natural gas  
21    which makes it difficult to transport safely and/or  
22    efficiently in its basic gaseous state. As a result

1 the natural gas is often flared (ignited) causing  
2 economic waste and environmental concern. It would  
3 therefore be desirable to either convert the natural  
4 gas into some other substance which can be  
5 transported easily, or transport the natural gas in  
6 a liquid state. In this way, new field development  
7 will be more financially viable through the use of  
8 the extensive infrastructure and technology already  
9 in place in the offshore industry for transporting  
10 liquid hydrocarbons.

11  
12 It is known to transport natural gas as a Liquid  
13 Natural Gas (LNG) in specifically constructed  
14 containers onboard vessels which have been adapted  
15 for such purposes. However, this has many  
16 disadvantages including; the need for expensive  
17 pressurising equipment which is difficult to scale  
18 down to suit smaller production fields, loss of gas  
19 during transportation ("boil-off"), danger posed in  
20 transit to vessel and crew by high pressure, highly  
21 flammable gases and the requirement to depressurise  
22 the LNG into a usable gaseous state at the customer  
23 end.

24  
25 It is considered that a better way of utilising  
26 offshore produced natural gas (CH<sub>4</sub>) is to convert  
27 it, on or in close proximity to the offshore  
28 production platform, into synthetic gas (syngas)  
29 which can in turn be used to produce gases, fluids  
30 and chemicals such as methanol, ammonia and  
31 importantly, crude oil that can be readily pumped  
32 through the same pipelines as the produced oil.

1 Syngas comprises a mixture of carbon monoxide(CO)  
2 and hydrogen(H<sub>2</sub>) .

3

4 By way of background information to the reader,  
5 conversion of syngas to liquid hydrocarbon is a  
6 chain growth reaction between carbon monoxide and  
7 hydrogen on the surface of a heterogeneous catalyst.  
8 The catalyst is either iron or cobalt based and the  
9 reaction is highly exothermic. The temperature,  
10 pressure, and catalyst determine whether a light or  
11 heavy syncrude is produced. For example at 330°C  
12 mostly gasoline and olefins are produced whereas at  
13 180°C to 250°C mostly diesel and waxes are produced.  
14 There are two main types of Fischer-Tropsch  
15 reactors. The vertical fixed tube type has the  
16 catalyst in tubes that are cooled externally by  
17 pressurised boiling water. In large plants, several  
18 reactors arranged in parallel may be used,  
19 presenting energy savings. Another process uses a  
20 slurry reactor in which pre-heated syngas is fed  
21 into the bottom of the reactor and distributed into  
22 the slurry which consists of liquid wax and catalyst  
23 particles. As the syngas bubbles upwards through  
24 the slurry, it is diffused and converted into more  
25 wax by the Fischer-Tropsch reaction. The heat  
26 generated is removed through the reactors cooling  
27 coils where steam is generated for use in the  
28 process. Again by way of background information to  
29 the reader, this is shown in Fig. 7.

30

31 Thus if methane (or other gaseous hydrocarbons)  
32 could be converted to syngas and thereafter to

1 liquid hydrocarbons, the transportation costs and  
2 difficulties outlined above would be mitigated.

3  
4 Synthesis gas can be made by partial oxidation of  
5 methane (although it is more usually made by the  
6 reaction of methane with steam under pressure.)

7  
8 A major safety problem with the partial oxidation of  
9 methane arises because methane and air (or oxygen)  
10 should be fed into the reactor at the same time and  
11 therefore there is the danger of an explosion.

12  
13 It is known in the art that a reactor with  
14 relatively dense ceramic membranes that conduct  
15 oxygen can be used for syngas production (e.g. WO  
16 98/48921 and WO 01/93987). These membranes generate  
17 syngas by avoiding direct contact between the oxygen  
18 and hydrocarbon feed, but this necessitates the use  
19 of very high temperatures in order to achieve the  
20 necessary oxygen flux. Moreover, being dense means  
21 that the membrane has to be as thin as possible,  
22 resulting in brittleness and crack formation, loss  
23 of efficiency and reduced operating service life.  
24 In some cases the membrane would need to be so thin  
25 that it would be unable to support its own weight  
26 and therefore impossible to use in practice.

27  
28 Cost effective natural gas (methane) conversion to  
29 syngas for gas-to-liquids production would therefore  
30 be an important commercial development.

31

1 Hydrogen can be used as a clean fuel. However, the  
2 amount of hydrogen that can be produced by using  
3 renewable natural energy sources such as solar,  
4 wind, and hydro-power is currently not sufficient to  
5 satisfy demand. The utilisation of natural gas  
6 and/or the production of hydrogen from natural gas  
7 seen to be a viable alternative and the most  
8 realistic solution at least in the first half of  
9 this century [1, 2].

10

11 An example of progress in the widespread utilisation  
12 of natural gas involves the development of small co-  
13 generation system using the micro-gas turbine. In  
14 addition, fuel cells are expected to be a highly-  
15 efficient power generating system. The fuel cells  
16 are anticipated to be deployed in residences in  
17 addition to the installation in electrical vehicles.  
18 Home-use of fuel cells can provide hot-water and  
19 electricity, simultaneously. To commercialise the  
20 stationary fuel cells, it is necessary to establish  
21 alternative hydrogen generation technology.

22

23 According to a first aspect of the present invention  
24 there is provided an apparatus comprising a first  
25 chamber and a second chamber and a membrane which  
26 divides the first and second chambers; the membrane  
27 comprising an inorganic support and a catalyst;  
28 the membrane being adapted to allow passage of a  
29 first reactant from the first chamber to the second  
30 chamber through said membrane;

1 wherein the first reactant is imparted with enough  
2 energy by the catalyst upon said passage so as to  
3 react with the second reactant.

4

5 According to a second aspect of the present  
6 invention there is provided a method of preparing a  
7 membrane, the method comprising:

8 providing a support; and  
9 adding a catalyst to the support.

10

11 Preferably the first reactant is activated by being  
12 imparted with enough energy by the catalyst upon  
13 said passage so as to react with the second  
14 reactant.

15

16 Preferably the energy imparted on the first reactant  
17 activates molecules of the first reactant without  
18 forming an ionic species, such as  $O^{2-}$ .

19

20 Preferably the support is adapted to operate at  
21 temperatures exceeding 250°C.

22

23 Preferably the support comprises an inorganic  
24 support.

25

26 Preferably, the membrane initially comprises an  
27 inorganic coarse porous support. Most preferably,  
28 the membrane initially comprises a ceramic coarse  
29 porous support such as alpha alumina.

30



1 Preferably, the first coating alters the said  
2 surface of the support and more preferably, the  
3 first coating roughens the said surface.

4  
5 Preferably, the first coating selectively alters the  
6 size, and more preferably, the diameter and  
7 tortuosity of the pores. Preferably, the first  
8 coating is applied by dipping the support into a  
9 solution which may comprise a wash coat solution  
10 such as a retracting metal oxide solution. In a  
11 preferred embodiment, the wash coat solution  
12 comprises Titanium Dioxide ( $\text{TiO}_2$ ). Typically, the  
13 first coating is applied to an outer surface which  
14 may be an outer cylindrical surface of the support.

15  
16 Typically, the method further includes the step of  
17 applying a second coating to a second surface of the  
18 support, said second surface preferably being an  
19 inner surface of the support and more preferably  
20 being an inner surface of a bore of the support.  
21 The second coating preferably comprises a flux  
22 control layer and more preferably the second coating  
23 is an inorganic porous layer. Most preferably, the  
24 second coating comprises a gamma alumina layer.  
25 Preferably, the second coating is applied by dipping  
26 the support into a solution which may comprise a  
27 boehmite solution.

28  
29 Typically, the method further includes the steps of  
30 drying the support and heating/firing the support.  
31 Typically, the dipping-drying-firing sequence of the

1 second coating may be repeated a number of times as  
2 required.

3  
4 Preferably, the method further includes the step of  
5 applying a catalyst to a surface of the membrane.  
6 Typically, the catalyst is applied to the inner bore  
7 of the pores of the membrane. Typically, the  
8 catalyst comprises a metallic or non-metallic  
9 catalyst, and is more preferably a metallic active  
10 catalyst. Most preferably, the catalyst comprises  
11 active rhodium. Alternatively the catalyst can  
12 comprise nickel. Preferably, the catalyst is  
13 applied to the said surface by passing an osmotic  
14 solution over the said first surface, which may be a  
15 first side, of the membrane and a cationic or  
16 anionic catalyst precursor solution over the said  
17 second surface, which may be the other side of the  
18 membrane, such that the catalyst is deposited on the  
19 inner bore of the membrane pores. Preferably, the  
20 osmotic solution comprises different electrolytes  
21 and non-electrolytes in an aqueous solution at room  
22 temperature. More preferably, the osmotic solution  
23 comprises a sucrose solution.

24  
25 Preferably, the method further includes the step of  
26 heating the membrane to a relatively high  
27 temperature and may include the further step of  
28 passing Hydrogen through the membrane pores such  
29 that calcination occurs.

30

1 Preferably, the support may comprise one or more  
2 inner structures such as struts to increase the  
3 surface area of the inner surface of the inner bore.  
4

5 According to a third aspect of the present invention  
6 there is provided a method of producing hydrogen  
7 gas, the method comprising:

8 providing a membrane, the membrane comprising a  
9 support and a catalyst;

10 passing a first reactant through the membrane  
11 from a first chamber to a second chamber; allowing  
12 the first reactant to come into contact with the  
13 catalyst upon passage through said membrane;

14 imparting the first reactant with enough energy  
15 so as to react with the second reactant;  
16 reacting the first reactant with a second reactant  
17 to produce hydrogen gas.  
18

19 Preferably, the membrane comprises a substantially  
20 annular cylinder and more preferably, the first and  
21 second chambers comprise a substantially cylindrical  
22 cross section. More preferably, a sidewall of the  
23 membrane separates the first and second chambers and  
24 the second cylindrical chamber may be located within  
25 the first cylindrical chamber.  
26

27 Preferably, the second cylindrical chamber is  
28 defined by an inner bore of the membrane.  
29

30 Preferably, a portion of the membrane is permeable.  
31 Alternatively, the entire membrane is permeable.  
32

1 Preferably, the first reactant passes from the first  
2 chamber through pores formed in the sidewall of the  
3 membrane to the second chamber.

4

5 Alternatively, the second reactant passes from the  
6 second chamber through the membrane to the first  
7 chamber.

8

9 Preferably, the first reactant is oxygen and the  
10 second reactant is a hydrocarbon. More preferably  
11 the second reactant is methane. Typically, the  
12 synthetic gas comprises carbon monoxide and  
13 hydrogen.

14

15 An embodiment of the present invention will now be  
16 described, by way of example only, with reference to  
17 the accompanying drawings in which:

18

19 Fig. 1 is a transverse cross sectional  
20 schematic view of a support of a membrane  
21 apparatus in accordance with the present  
22 invention;

23 Fig. 2A is a transverse cross sectional view  
24 showing the support of Fig. 1 in more detail;  
25 Fig. 2B is an end view of the support of Fig.  
26 2A showing 'O' rings and cross sectional shape  
27 of the support;

28 Fig. 3a is a diagrammatic cross sectional view  
29 showing the formation of layers in the membrane  
30 of the membrane apparatus of Figs. 2A and 2B;  
31 Fig. 3b is a further diagrammatic cross  
32 sectional view of the membrane apparatus;

1        Fig. 3c is a yet further diagrammatic cross  
2        sectional view of the membrane apparatus  
3        showing the movement of molecules in use;  
4        Fig. 4 is a temperature / syngas ratio plot  
5        showing the optimal temperature required to  
6        achieve the desired syngas ratio;  
7        Fig. 5 is a feed ratio / syngas ratio plot  
8        showing the optimal feed ratio required to  
9        achieve the desired syngas ratio; and  
10       Fig. 6 is a % Vol. N<sub>2</sub> / Conversion plot showing  
11       conversion of CH<sub>4</sub> and O<sub>2</sub> at 750°C;  
12       Fig. 7 is a schematic flow diagram providing  
13       background information relating to Fischer-  
14       Tropsch Gas-to-Liquids Technology;  
15       Fig. 8a is a graph showing the effect of  
16       temperature on the methane conversion rate;  
17       Fig. 8b is a graph showing the effect of  
18       reaction temperature on the conversion rate of  
19       methane for fixed-bed and membrane reactors;  
20       Fig. 9 is a graph showing the yield of reaction  
21       products at low methane conversation rates for  
22       a membrane apparatus in accordance with the  
23       present invention;  
24       Fig. 10 is a graph showing the yield of various  
25       reaction products at high methane conversion  
26       rates by varying the feed ratio at a fixed  
27       temperature;  
28       Fig. 11 is a graph showing the yield of various  
29       reaction products by varying the temperature at  
30       a fixed feed ratio;

1           Fig. 12 is a graph showing the selectivity of  
2           various reaction products at low methane  
3           conversions;  
4           Fig. 13 is a graph showing the selectivity of  
5           various reaction products by varying the feed  
6           ratio at a fixed temperature;  
7           Fig. 14 is a graph showing the selectivity of  
8           various reaction products by varying the  
9           temperature at a fixed feed ratio;  
10          Fig. 15 is a graph showing the yield of various  
11          reaction products against the proportion of  
12          nitrogen in a nitrogen/oxygen feed;  
13          Fig. 16 is a graph showing the selectivity of  
14          various reaction products against the  
15          percentage of nitrogen in the nitrogen/oxygen  
16          feed.  
17          Fig. 17 is a graph showing the yield of various  
18          reaction products against the percentage of  
19          carbon dioxide in the methane feed; and,  
20          Fig. 18 is a graph showing the selectivity of  
21          various reaction products against the  
22          percentage of carbon dioxide in the methane  
23          feed.

24

25          A membrane apparatus 8 in accordance with the  
26          present invention is shown in Fig. 1 and comprises a  
27          tubular membrane 10 and an outer tubular shell 16.  
28          Two gas flow passages are thus formed which are  
29          substantially sealed off from each other. The first  
30          within a bore 14 of the membrane 10 and the second  
31          in the annulus 22 between the membrane 10 and the  
32          shell 16.

1 The inner bore 14 of the modified membrane 10 may  
2 have some supporting struts 34, as shown in Fig. 2.  
3 These increase the structural strength of the  
4 modified membrane 10. In operation, the struts 34  
5 also change the flow pattern of oxygen flowing  
6 through the sidewall 13 of the membrane 10 by  
7 reducing the opportunity for the methane flowing  
8 through the inner bore 14 to pass directly through  
9 the centre of the modified membrane 10 inner bore  
10 without coming into contact with the modified  
11 membrane 10 surface. The struts 34 also increase  
12 the internal surface area per unit volume of the  
13 modified membrane 10, and hence increase the  
14 opportunity for activation, compared to a completely  
15 hollow cross section.

16  
17 With reference to Fig. 3c, the modified membrane 10  
18 comprises an  $\alpha$ -alumina support 10, a  $\text{TiO}_2$  washcoat  
19 28 on the outer surface of the support 10 and a  
20  $\gamma$ -alumina layer 30 on the inside of the  $\alpha$ -alumina  
21 support 10. Rh catalyst particles 12 are  
22 impregnated into the bores of the inner and outer  
23 face of the sidewall 13 of the modified membrane 10.

24  
25 Further layers of increasing pore radii may be  
26 provided adjacent to the  $\gamma$ -alumina layer 30 and  $\text{TiO}_2$   
27 28 layers.

28  
29 Referring to Figs. 2A, 2B and 3a-3b the preparation  
30 of the membrane 10 layers will now be described.

31

1 The process starts with the inorganic (preferably  
2 ceramic) coarse porous support 10. Supports of this  
3 nature are now widely available and a wide variety  
4 of companies currently supply these base materials  
5 and a preferred support 10 comprises an alpha-  
6 alumina tube having 10mm outer diameter and a 7mm  
7 inner diameter, typically having a pore size of  
8 between 110 and 180 nm. The support 10 comprises a  
9 porous middle portion 11 which is typically around  
10 300 mm in length, and two remaining non-porous  
11 portions 26 of about 25 mm in length at each end of  
12 the membrane 10. The end portions 26 are made non-  
13 porous by glazing them with a sealant, such as  $\text{SiO}_2$ -  
14  $\text{BaO-CaO}$  at 1100°C.

15  
16 The wash coat 28 is then applied to the outer  
17 cylindrical surface of the support 10 by dipping the  
18 support 10 into a substance such as  $\text{TiO}_2$ . This wash  
19 coat 28 dipping step roughens the outer cylindrical  
20 surface of the support 10 and adds microporosity to  
21 the walls of the membrane catalysts 12. (In  
22 operation the rough surface of the wash coat 28  
23 forces the oxygen particles (not shown) to convolute  
24 around the raggedness of the wash coat 12 and serves  
25 to improve mass transfer of the limiting reactant  
26 (oxygen) to the catalytic sites - this results in  
27 improved syngas yields).

28  
29 The oxygen flux control layer 30 is then applied to  
30 the inside surface of the inner bore 14 of the  
31 support 10. This layer 30 should be inorganic to  
32 enable operation of the membrane 10 at high



1 temperatures and may comprise a gamma alumina layer  
2 derived from a boehmite( $\text{AlO}(\text{OH})$ ) solution with a  
3 concentration of 0.6 mol/L. The inner surface of  
4 the support 10 is exposed to the boehmite solution  
5 via dipping for about 2 minutes. The support is  
6 then air-dried overnight and then heated to between  
7 700 - 750°C at a rate of 1°C / min. It may be  
8 necessary to repeat this dipping-drying-firing  
9 sequence for up to a total of three cycles to  
10 achieve the required gamma-alumina layer thickness  
11 on the support 10.

12  
13 The deposition of the catalysts 12 on the support 10  
14 is achieved using an osmotic ionic exchange process,  
15 which will now be described.

16  
17 Osmotic Ionic Exchanged Catalyst Deposition:

18  
19 The catalysts 12 are prepared using either cationic  
20 or anionic exchange using  $\text{RhNO}_3$  or  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$   
21 respectively in an organic medium (0.2g/L) as  
22 precursors. Owing to the asymmetrical character of  
23 the membrane as shown in Fig. 3a (i.e. wash coat 28  
24 + support 10 + gamma alumina layer (boehmite) 30)  
25 different ways of introducing the catalysts 12 to  
26 the support 10 are utilised. In the first instance,  
27 the osmosis process involves immersing the outer  
28 surface of the partially modified membrane 10 in 6.0  
29 molar sucrose solution, while the catalyst precursor  
30 solution (e.g.  $\text{RhNO}_3$  or  $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ ) is circulated  
31 through the inner bore 14 of the partially modified  
32 membrane 10. This configuration is reversed in the

1 second instance with the immersion of the outer  
2 surface of the partially modified membrane 10 now in  
3 a catalyst precursor solution and the osmotic  
4 (sucrose) solution now circulated in the inner bore  
5 14 of the partially modified membrane 10. The  
6 membrane 10 is then washed using distilled water and  
7 subsequently dried by blowing dry air either through  
8 the inner bore of the now modified membrane 10 or  
9 across the outer cylindrical surface.

10

11 Calcination (which involves heating the modified  
12 membrane 10 to a very high temperature and then  
13 passing Hydrogen through the modified membrane 10)  
14 is then carried out under atmospheric pressure at  
15 400°C for 2 hours. Metallic (active) Rh (the  
16 catalyst 12) is obtained by reduction of Rhodium  
17 ionic species using hydrogen at 400°C for 2 hours.

18

19 The modified membrane 10 characteristics may now be  
20 measured. This may be done by scanning electron  
21 microscopy (SEM) to show the degree of filling of  
22 the modified membrane 10 pore network and to  
23 estimate the gamma alumina (boehmite) layer 30  
24 thickness.

25

26 Alternative materials may be selected. However it  
27 is important that the selected materials have  
28 similar thermal coefficients of expansion as  
29 adjacent layers. If there is difference in thermal  
30 expansion coefficients of the active porous layers  
31 and porous support layers, there is an advantage in  
32 selecting materials for the intermediate porous

1 support layers, with expansion coefficients which  
2 gradually change from values near those for the  
3 active porous layer to values near those for the  
4 outer porous support layer. One way of achieving  
5 this is to prepare the intermediate layers from a  
6 mixture of the material used in forming active  
7 porous layer decreasing in successive porous support  
8 layers. For instance, porous support layer could  
9 contain 75% by weight of the material used in  
10 forming the active porous layer.

11  
12 The above discussion does not exclude the use of  
13 identical materials in active porous layer and  
14 porous support layer. Such a material selection will  
15 eliminate chemical incompatibility and differential  
16 thermal expansion problems but typically entails  
17 sacrifices in strength and material cost.

18  
19 The number of porous support layers will depend on  
20 the porous radius of the adjacent active porous  
21 layer. They will vary from a single layer for  
22 active porous layer pore radii selected from the  
23 upper end of the specified range to four for pore  
24 radii selected from the lower end of the specified  
25 range.

26  
27 The surface area of a material determines many of  
28 its physical and chemical properties, including  
29 water retention capacity and reactivity with  
30 nutrients and contaminants. The BET Surface Area  
31 Analyser can be used to estimate the specific  
32 external surface of a solid by determining the

1 volume of a specific gas that is absorbed under  
2 controlled conditions. The BET surface Area  
3 Analyser has typically been used in routine  
4 characterisation of various membrane materials and  
5 synthetic mineral analogues important in process  
6 engineering systems.

7  
8 In the context of the present invention, BET surface  
9 area analysis using nitrogen adsorption is used to  
10 estimate the pore size distribution in the modified  
11 membrane 10 and also to indicate values of porosity  
12 and pore volume. Energy Dispersive X-Ray Analysis  
13 (EDXA) surface analysis of the modified membrane 10  
14 is used to confirm whether or not the modified  
15 membrane 10 forms a continuous gamma alumina network  
16 and the extent of any defects. It also provides  
17 elemental composition of the catalysts 12 and its  
18 relative dispersion. X-ray Photoelectron  
19 Spectroscopy (XPS) is then used for chemical  
20 analysis of the modified membrane 10.

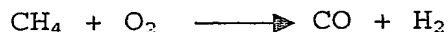
21  
22 It is recognised that the partial oxidation of  
23 methane may occur via two distinct mechanisms, i.e.  
24 direct partial oxidation or total oxidation followed  
25 by reforming reactions.

26  
27 To convert methane to syngas a partial oxidation is  
28 required.

29

30

31



32

1 Should a full oxidation occur, the reaction products  
2 would be CO<sub>2</sub> and H<sub>2</sub>O.

3

4 The operation of the modified membrane 10 in the  
5 membrane apparatus 8 will now be described.

6

7 An oxygen (O<sub>2</sub>) supply 18 is fed into the outer bore  
8 22 at one end of the membrane apparatus 8, and a  
9 natural gas (which mainly comprises methane (CH<sub>4</sub>))  
10 supply 20 is fed into the corresponding end of the  
11 inner bore 14.

12

13 The partial pressure of the oxygen 18 is maintained  
14 at a higher pressure than that of the methane supply  
15 20, which results in the oxygen passing through the  
16 pores (not shown) of the modified membrane 10 from  
17 the outer bore 22 to the inner bore 14. Upon doing  
18 so, the oxygen molecules come into contact with the  
19 catalysts 12 present in the sidewall 13 of the  
20 modified membrane 10, which activates the oxygen  
21 molecules before contacting the methane present in  
22 the inner bore of the modified membrane 10. This  
23 activation imparts sufficient energy on the O<sub>2</sub>  
24 molecule so that it can react at relatively low  
25 temperatures without forming an oxygen ion.

26

27 When the activated oxygen molecules come into  
28 contact with the methane molecules, syngas is  
29 instantly formed according to the following chemical  
30 reaction:-

31

32  $\text{CH}_4 + \text{O}_2^* \Rightarrow_{\text{catalyst}} \text{CO} + \text{H}_2.$

1 The produced syngas exits the membrane apparatus 8  
2 from the other end of the inner bore 14 due to the  
3 natural pressure differential created by the methane  
4 supply 20, such that a syngas flow 24 is created.  
5 Pneumatic control of the oxygen supply 18 flow rate  
6 allows different flow rates of the methane supply 20  
7 to be used, since an increase in the pressure of the  
8 oxygen supply will result in a greater flux of  
9 oxygen through the pores of the modified membrane  
10 10.

11

12 In use a gas stream comprising the methane flows  
13 next to or through the catalyst impregnated layer  
14 12. The gamma alumina layer 30 on the bore side 14  
15 enhances the reaction between permeated oxygen and  
16 the methane. Since the oxygen molecules have to  
17 diffuse to the bore side 14 of the gamma alumina  
18 layer 30 and the adjacent porous layer, the gaseous  
19 environment of the gamma alumina layer 30 at and  
20 near the bore is less reducing than in the outer  
21 porous layers. As a result a complete or partial  
22 oxidation reaction will take place here with some  
23 reforming occurring as gas moves away from the gamma  
24 alumina layer 30 respectively. It is advantageous to  
25 coat pores of the last porous support layer with the  
26 reforming catalyst such as Rh to induce some  
27 endothermic reforming as combustion products flow  
28 through the porous support layer. This will assist  
29 in removing the heat of the exothermic oxidation  
30 reaction from the surface of the active porous  
31 layer.

32

1 The gradient in oxygen activity in the porous layer  
2 will prevent damage to the gamma alumina layer 30  
3 from exposure to very low oxygen partial pressures,  
4 thus permitting a greater degree of freedom in the  
5 selection of materials for these layers.

6  
7 Gas permeability through the modified membrane 10  
8 can be measured by placing the end of the modified  
9 membrane 10 sample tightly against the ends of the  
10 outer tubular shell 16, with a seal being formed  
11 therebetween by 'O' rings 32. A gas connection (not  
12 shown) of the outer tubular shell 16 is attached to  
13 a source of constant pressure. The predetermined  
14 pressure difference being used creates a stable flow  
15 of gas through the sidewall 13 of the membrane 10  
16 sample, and is used to measure the flow rate, which  
17 is proportional to the gas permeability of the  
18 modified membrane 10.

19  
20 Multi-component selectivity can be obtained by  
21 measuring the individual species concentration in  
22 the feed and permeate respectively.

23  
24 Analysis of the reactants and products are analysed  
25 using gas chromatography (GC) on-line using a 5 m  
26 1/8 inch molecular sieve column to determine  
27 methane, O<sub>2</sub>, H<sub>2</sub> and CO. Any CO<sub>2</sub> will be analysed  
28 using a separate 2 m long column of Porapak (RTM)  
29 QS. In this analysis, a thermal conductivity  
30 detector is also used. Water formed during the  
31 reaction is condensed in an ice trap and further  
32 removed by using a Drierite (RTM) trap.

1 In order to calibrate the chromatograph, multi-  
2 component gas mixtures consisting of certified  
3 compositions of methane, hydrogen, carbon dioxide,  
4 carbon monoxide and oxygen were fed on one side of  
5 the modified membrane 10 (e.g. the outer bore 22)  
6 and the streams entering and exiting the inner bore  
7 14 were analysed using the Thermal Conductivity  
8 Detector (TCD) of a gas chromatograph.

9  
10 Other aspects investigated in testing the membrane  
11 10 include the effect of operating temperature (Fig.  
12 4), methane flow rate (Fig. 5) and composition of  
13 syngas yield and selectivity (Figs. 4 and 6).

14  
15 Figs. 9-18 show a variety of these results using  
16 such an apparatus. In each case, values of oxygen  
17 and methane conversions and the yields of hydrogen  
18 and carbon monoxide are monitored.

19  
20 To investigate the initial reaction products of the  
21  $\text{CH}_4/\text{O}_2$  feed, experiments were carried out at low  
22 methane conversion rates and the products were  
23 analysed as detailed above.

24  
25 The oxygen feed flow rate was held constant at  
26 75ml/min and the methane feed flow rate was varied  
27 from 150 to 425ml/min, giving a range of total feed  
28 flow rates from 225 to 500ml/min. The higher total  
29 feed flow rate decreases the contact time of the  
30 reactants with the catalysts, thereby decreasing  
31 methane conversation.

32



1 In Fig. 8 it can be observed that for methane  
2 conversion above and below 15% the CO<sub>2</sub> yield  
3 increases significantly.

4  
5 The CO yield by contrast, increases for conversions  
6 lower than 20% having a slight decrease at  
7 conversions around 16% increasing again thereafter.  
8 The average CO yield is the highest average yield of  
9 any one product. The water yield follows the same  
10 profile as that for CO, but for methane conversions  
11 around 18% it decreases again, deviating from the CO  
12 yield. The average water yield is the lowest average  
13 yield of any one product. The hydrogen yield is a  
14 mirror image of the CO yield up to 16% methane  
15 conversion, rising considerably for higher  
16 conversion rates.

17

18 In a second experiment, the feed flow rate of oxygen  
19 was varied from 15-75ml/min whilst the flow rate of  
20 the methane was held constant at 150ml/min giving  
21 reactions with total flow rates from 165-225ml/min,  
22 as shown in Fig. 9. The temperature was 1023.15K.  
23 The methane conversion decreases proportionally with  
24 the increase in total flow rate, i.e. with the  
25 decrease in contact time.

26

27 With higher methane conversions rates, allowing more  
28 contact time, the CO<sub>2</sub> yield continues to increase up  
29 to 30% methane conversion, falling slightly around  
30 15% yield and significantly when methane conversions  
31 reach around 50%. When methane conversion is over  
32 55%, an insignificant yield of 5% CO<sub>2</sub> is found. Thus

1 the lowest yield of CO<sub>2</sub> is found for methane  
2 conversion higher than 50%.

3  
4 The CO yield stabilises at around 15% for methane  
5 conversions higher than 20%. Water yield stabilises  
6 at 5% for methane conversion from 20% up to around  
7 40% increasing to almost 10% water yield at around  
8 50% methane conversion, falling again to around 5%  
9 yield at 55% methane conversion. Hydrogen yield  
10 rises to around 18% hydrogen for methane conversions  
11 from 30% up to 50% declining to 0.16 yield for  
12 higher methane conversions.

13  
14 Thus the contact time (controlled by the feed rate)  
15 does not have a significant influence on the  
16 resulting products, but does influence the methane  
17 conversion rate. An advantage of certain  
18 embodiments of the present invention is that they  
19 can be used with low and high flow rates (producing  
20 corresponding high and low contact times) without  
21 affecting the resulting products. Longer contact  
22 times aid methane conversion and provides high  
23 yields of hydrogen and carbon monoxide and low  
24 yields of water and carbon dioxide with methane  
25 conversion is at about 50%.

26  
27 To obtain this contact time the total feed flow rate  
28 needs to be lower than 185ml/min for this load of  
29 catalyst and temperature of 1023.15K. Other  
30 embodiments of the invention can use different feed  
31 flow rates.

32

1 It is well recognised that the partial oxidation of  
2 methane may occur via two distinct mechanisms, i.e.,  
3 direct partial oxidation or total oxidation followed  
4 by reforming reactions [3]. In order to elucidate  
5 the mechanism for the catalytic membrane reactor  
6 used here, the effect of the temperature on the  
7 methane conversion and product yields was studied.  
8 The results of the analysis are presented in Figures  
9 4 and 8a.

10

11 Fig. 8a shows the influence of temperature on  
12 methane conversion and products yields for a total  
13 feed flow rate of 165ml/min (150ml/min of methane  
14 and 15ml/min of oxygen). Figure 8a shows that all  
15 the oxygen is consumed. This occurs before  
16 significant amounts of hydrogen and carbon monoxide  
17 are formed. Another important feature is that the  
18 conversion of methane, yield of water and yield of  
19 hydrogen all pass through a maximum at 750°C. This  
20 behaviour suggests that below 750°C, water, carbon  
21 monoxide and hydrogen are primary products while  
22 carbon dioxide is a parallel side reaction as  
23 depicted in scheme 1.

24

25

26

27

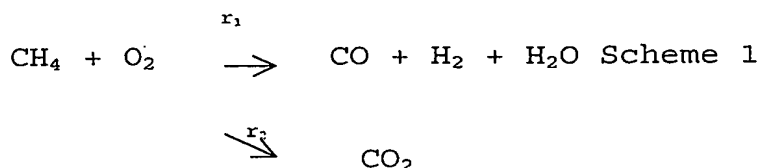
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29

30

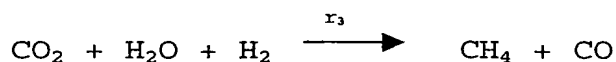
31

32



Kinetic modelling has shown that the overall  
reaction can be described well with the contribution  
of parallel oxidation and full oxidation according  
to scheme 1.

Above 750°C, the total oxidation reaction  $r_2$  is expected to dominate with a significant increase in water and carbon dioxide. However, examination of Figure 8a shows that the carbon dioxide yield shows only a modest increase above 750°C, while the yields for water and hydrogen fall above this temperature. This suggests that hydrogen, carbon dioxide and water are being consumed accordingly to scheme 2 below.



Scheme 2

Scheme 2 helps explain the fall in the water and hydrogen yields, the modest  $\text{CO}_2$  yield increase and the fall in methane conversion above 750°C.

One important aspect in the subsequent conversion of synthesis gas to liquids via a Fischer-Tropsch type reaction is the hydrogen: carbon monoxide ratio. A ratio of 2/1 is optimum for this conversion. From examination of Fig. 4 it can be seen that an optimal temperature of around 750°C results in the desired syngas ( $\text{H}_2/\text{CO}$ ) ratio of 2.

The optimal feed ratio of methane to oxygen is shown, in Fig. 5, to be 10, although reasonable results which are relatively close to the desired ratio of 2 are obtained at feed ratios of between 2 and 6 also.

1 Figure 4 shows a plot of the  $H_2/CO$  over the  
2 temperature range studied. The optimum for gas-to-  
3 liquids conversion is obtained at a temperature of  
4  $750^{\circ}C$ . Above this temperature, a ratio below 2.0 is  
5 attained while below  $750^{\circ}C$ , a value above 2.0 is  
6 obtained.

7  
8 Selectivity is defined as the yield of a particular  
9 component in proportion to the amount of methane  
10 conversion, that is

11  
12 
$$\text{Selectivity}_x = \text{Yield}_x / \text{Conversion}_{CH_4}$$

13  
14 Selectivity for low and high methane conversion  
15 rates is shown in Figs. 12 and 13. There the CO  
16 selectivity remains almost constant with values  
17 around 0.9. This possibly indicates the absence of  
18 secondary reactions for CO in low methane  
19 conversions. Hydrogen selectivity decreases for  
20 methane conversion up to 15% and increases  
21 thereafter, reaching similar CO selectivity values.

22  
23 Water selectivity profile follows a mirror image of  
24 hydrogen selectivity, increasing for conversions up  
25 to 15%, decreasing for higher conversions. For  
26 higher values of methane conversion water  
27 selectivity is constant, indicating the absence of  
28 secondary reactions for water formation.

29  
30 Hydrogen selectivity decreases significantly for  
31 methane conversions up to 50%, increasing slightly  
32 after that.

1 The selectivity of CO decreases to lower values than  
2 H<sub>2</sub> selectivity for methane conversions up to 45%  
3 becoming stable thereafter, indicating that for  
4 methane conversions higher than 46%, CO is not  
5 formed by any secondary reaction.

6  
7 CO<sub>2</sub> selectivity decreases with the increase of  
8 methane conversion, being the least selective gas  
9 formed in this reaction.

10

11 It is important to note that the above-mentioned  
12 experimental data were taken with varying contact  
13 time, which can influence on the selectivity values.  
14 For constant contact time, but varying temperature,  
15 values are shown in Fig. 14.

16

#### 17 **Effect of Feed Composition Variation on Reactor** 18 **Performance**

19

20 Figs. 15 and 16 show the yield and selectivity when  
21 a varying proportion of nitrogen is added to the  
22 oxygen feed. This influences the contact time of the  
23 reagents with the catalyst.

24

25 Fig. 15 shows that CO yield falls constantly with  
26 the addition of nitrogen in the system. Hydrogen  
27 yield decreases with up to 50% nitrogen in the  
28 oxygen feed and is constant thereafter.

29

30 The selectivity of carbon dioxide and water as shown  
31 in the yield chart is not affected by the addition  
32 of nitrogen in the system. However carbon monoxide

1 and hydrogen selectivities have a continuous drop  
2 after a pick up at around 50% vol. of nitrogen.

3  
4 The water and CO<sub>2</sub> yields values do not differ  
5 significantly when nitrogen is present or absent  
6 although there is a small rise for air composition  
7 (80% N<sub>2</sub>).

8  
9 Fig. 6 also shows that even for an 80% vol N<sub>2</sub> feed  
10 (and hence 20% O<sub>2</sub> feed) total oxygen conversion  
11 takes place at a temperature of 750°C. The results  
12 show that embodiments of the present invention can  
13 work by using an air feed rather than a pure oxygen  
14 feed thereby negating the need for an oxygen  
15 separation plant for this reaction to take place.  
16 This clearly reduces both the initial outlays and  
17 operating costs of performing the reaction. Thus a  
18 benefit of certain embodiments of the invention is  
19 that air separation is not required to produce the  
20 syngas of optimal ratio for onward reaction to  
21 liquid hydrocarbons via a Fischer-Tropsch reaction.

22  
23 In contrast to the nitrogen, the addition of CO<sub>2</sub> in  
24 the feed does not influence CO yield, but reduces  
25 hydrogen yield whilst increasing H<sub>2</sub>O yield. The  
26 results are shown in Figs. 17 and 18.

27  
28 The selectivity of CO and H<sub>2</sub> decreases slightly in  
29 higher proportion for hydrogen with the addition of  
30 CO<sub>2</sub> in the methane feed.

31

1 The water selectivity is generally constant but does  
2 increase slightly for higher amounts of CO<sub>2</sub> in the  
3 feed.

4  
5 An advantage of certain embodiments of the invention  
6 is that the oxygen and methane are fed separately  
7 into the apparatus and so there is no danger of an  
8 explosion. The oxygen proceeds through the modified  
9 membrane 10, is activated and then reacts when it  
10 comes into contact with the methane. Thus it is  
11 possible to lower the ratio of methane and oxygen in  
12 the feed to a ratio more suitable for their  
13 reaction. Such a ratio would normally be considered  
14 potentially explosive, but certain embodiments of  
15 the present invention allow for such ratios without  
16 the potential for an explosion partly because of the  
17 separate oxygen/methane feed.

18  
19 Embodiments of the present invention benefit from  
20 the highly dispersed catalyst which increase its  
21 surface area and efficacy of the apparatus.

22  
23 Embodiments of the present invention benefit from  
24 the high conversion rate of oxygen. To illustrate  
25 the benefits of membrane reactor operation in syngas  
26 production, Figure 8b shows the effect of reaction  
27 temperature on the conversion of methane over Ir-  
28 loaded catalyst carried out with fixed-bed flow type  
29 quartz reactor (350-10mm) at atmospheric pressure,  
30 using 60mg of catalyst, 25 ml/min of O<sub>2</sub> and  
31 temperature range of 673-873K. At 873K the  
32 performance of Ir and Rh are roughly identical [4].



1 In the same figure, experimental data is shown for a  
2 membrane system in accordance with the present  
3 invention at 900.15K. The conversion values obtained  
4 using a fixed-bed flow reactor are significantly  
5 lower than those obtained in the membrane reactor  
6 due to equilibrium limitation. This has been  
7 overcome in the membrane reactor which achieves 100%  
8 conversion of oxygen and a methane conversion of  
9 41%.

10

11 Since, in the modified membrane 10, the catalysts 12  
12 are highly dispersed, lower reaction temperatures  
13 are feasible thereby reducing the propensity for  
14 coke formation and subsequent deactivation of the  
15 catalysts 12. The absence of coke formation  
16 optimises catalyst usage whilst maintaining high  
17 syngas selectivity. In the operation of the  
18 membrane apparatus 8, additional catalysts (not  
19 shown) may be inserted into the inner bore of the  
20 modified membrane 10 as necessary to further enhance  
21 the reaction. These additional catalysts (not  
22 shown) are obtained by physically breaking another  
23 sample of a modified membrane 10 into appropriate  
24 particle sizes and inserting the particle sizes into  
25 the test or operation sample.

26

27 Certain embodiments of the present invention benefit  
28 from being used to generate hydrogen from, for  
29 example, methane. The hydrogen can be used as a  
30 fuel itself rather than converted into larger  
31 hydrocarbons via a Fischer-Tropsch reaction.

32

1 Certain embodiments of the invention benefit from  
2 the fact that the partial oxidation method is  
3 exothermic and therefore reduces energy consumption.

4  
5 Certain embodiments of the invention benefit from  
6 the fact that the process has a fast start-up.

7  
8 In contrast, steam reforming to produce syngas has a  
9 large endothermic reaction and a slow start-up time.

10  
11 Thus certain embodiments of the invention provide a  
12 catalytic membrane reactor which has been developed  
13 and used to produce hydrogen, particularly synthesis  
14 gas; under various operating conditions with total  
15 consumption of oxygen. At lower feed ratios ( $\text{CH}_4/\text{O}_2$ ),  
16 the syngas ratio is well above 2.0 while at higher  
17  $\text{CH}_4/\text{O}_2$  ratio, the syngas ratio is 2.0. Thus depending  
18 on the application the reactor is flexible to the  
19 extent that it could be applied in the Fischer-  
20 Tropsch process for converting natural gas to liquid  
21 hydrocarbons. For gas-to-liquids conversion, an  
22 optimum temperature of  $750^\circ\text{C}$  has been established at  
23 which the hydrogen/carbon monoxide ratio is 2.0.

24  
25 Modifications and improvements may be made to the  
26 foregoing without departing from the scope of the  
27 present invention. For example;

28  
29 Though the apparatus and method described relates to  
30 the production of syngas from the reaction between  
31 methane and oxygen, a similar method and apparatus  
32 could be used in the reaction of any light

1 hydrocarbon such as members of the alkane or alkene  
2 group. Furthermore, the process and apparatus could  
3 be used in any reaction where there are two  
4 reactants which have constraints that make it  
5 undesirable to mix them before the reaction has  
6 taken place, such as flammability constraints.

7  
8 It will be understood that the flux of oxygen could  
9 be reversed by feeding the oxygen into the bore of  
10 the modified membrane 10, and the methane into the  
11 outer bore 22. However, in this case this  
12 arrangement would be less desirable since the  
13 methane may have impurities in it, such as  $H_2S$ ,  
14 which would poison the catalyst 12. Therefore  
15 passing the oxygen through the modified membrane 10  
16 is preferred.

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9              *Methane to Synthesis Gas with Iridium-loaded*  
10             *Titania Catalyst*. *Chemistry Letters*, 1996: p.  
11             1029-1030.
- 12

## 1    Claims

2

3    1.    An apparatus comprising a first chamber and a  
4           second chamber and a membrane which divides  
5           the first and second chambers; the membrane  
6           comprising a support and a catalyst;  
7           the membrane being adapted to allow passage of  
8           a first reactant from the first chamber to the  
9           second chamber through said membrane;  
10          wherein the first reactant is imparted with  
11          enough energy by the catalyst upon said  
12          passage so as to react with the second  
13          reactant.

14

15    2.    Apparatus as claimed in claim 1, wherein the  
16          support is adapted to operate at temperatures  
17          exceeding 250°C.

18

19    3.    Apparatus as claimed in claim 2, wherein the  
20          support comprises an inorganic support.

21

22    4.    Apparatus as claimed in any preceding claim,  
23          wherein the support comprises pores and there  
24          is a gradation in the average pore radii  
25          towards one surface of the support.

26

27    5.    Apparatus as claimed in any preceding claim,  
28          wherein the membrane is adapted to activate  
29          molecules of the first reactant without  
30          forming an ionic species before the reaction  
31          with the second reactant.

32

- 1    6.    Apparatus as claimed in any preceding claim,  
2        wherein the support comprises a layer with a  
3        roughened surface which has an increased  
4        tortuosity compared to the tortuosity of the  
5        rest of the support.  
6
- 7    7.    Apparatus as claimed in claim 6, wherein the  
8        relatively roughened surface is provided on an  
9        outer surface of the support.  
10
- 11
- 12   8.    Apparatus as claimed in any preceding claim,  
13        wherein a flux control layer is provided on  
14        the support.  
15
- 16   9.    An apparatus as claimed in any one of claims 6  
17        or 7, wherein a flux control layer is provided  
18        on a first surface of the support and the  
19        layer with a roughened surface is provided on  
20        an opposite surface of the support.  
21
- 22   10.   Apparatus as claimed in claim 8 or 9, wherein  
23        the flux control layer comprises an inorganic  
24        porous layer which is adapted to hold a  
25        portion of the catalyst therein and to control  
26        the passage of the first reactant through the  
27        membrane.  
28
- 29   11.   Apparatus as claimed in any one of claims 8 to  
30        10, wherein the flux control layer is selected  
31        from the group consisting of silica and gamma  
32        alumina.

1 12. Apparatus as claimed in any preceding claim,  
2 wherein the catalyst comprises a metal  
3 catalyst.  
4

5 13. Apparatus as claimed in claim 12, wherein the  
6 metal catalyst is selected from the group  
7 consisting of rhodium, ruthenium and nickel.  
8

9 14. Apparatus as claimed in any preceding claim,  
10 wherein the membrane is provided in the shape  
11 of a cylinder.  
12

13 15. Apparatus as claimed in any preceding claim,  
14 wherein the membrane comprises one or more  
15 struts.  
16

17 16. Apparatus as claimed in any preceding claim,  
18 wherein the support comprises alpha alumina.  
19

20 17. A method of producing hydrogen gas, the method  
21 comprising:  
22 providing a membrane, the membrane comprising  
23 a support and a catalyst;  
24 passing a first reactant through the membrane  
25 from a first chamber to a second chamber;  
26 allowing the first reactant to come into  
27 contact with the catalyst upon passage through  
28 said membrane;  
29 imparting the first reactant with enough  
30 energy so as to react with the second  
31 reactant;

1            reacting the first reactant with a second  
2            reactant to produce hydrogen gas.

3

4    18.    A method as claimed in claim 17, wherein the  
5            energy imparted on the first reactant  
6            activates molecules of the first reactant  
7            without forming an ionic species before the  
8            reaction with the second reactant.

9

10   19.    A method as claimed in claim 17 or 18, wherein  
11           the temperature is over 500°C.

12

13   20.    A method as claimed in claim 19, wherein the  
14           temperature is between 700°C and 800°C.

15

16   21.    A method as claimed in any one of claims 17 to  
17           20, wherein the first reactant is one of  
18           oxygen and a hydrocarbon, and the second  
19           reactant is the other of oxygen and a  
20           hydrocarbon.

21

22   22.    A method as claimed in claim 21, wherein the  
23           oxygen and hydrocarbon do not come into  
24           contact with each other until the first  
25           reactant has passed through said membrane from  
26           the first chamber to the second chamber.

27

28   23.    A method as claimed in claim 21 or 22, wherein  
29           the hydrocarbon comprises a normally gaseous  
30           hydrocarbon.

31



1 24. A method as claimed in any one of claims 20 to  
2 23, wherein the pressure within the first  
3 chamber is greater than the pressure within  
4 the second chamber.

5

6 25. A method as claimed in any one of claims 20 to  
7 24, wherein carbon monoxide is formed in  
8 addition to the hydrogen.

9

10 26. A method as claimed in claim 25, wherein the  
11 carbon monoxide and hydrogen are further  
12 reacted to produce normally liquid  
13 hydrocarbons in a Fischer-Tropsch type  
14 reaction.

15

16 27. A method as claimed in any one of claims 20 to  
17 25, wherein the hydrogen is recovered for use  
18 as a fuel.

19

20 28. A method of preparing a membrane, the method  
21 comprising:  
22 providing a support; and  
23 adding a catalyst to the support.

24

25 29. A method as claimed in claim 28, wherein the  
26 support is an inorganic support.

27

28 30. A method as claimed in claim 28 or 29, further  
29 including the step of applying a coating to  
30 one of the surfaces of the support.

31

- 1 31. A method as claimed in claim 30, wherein the  
2 coating produces a roughened surface on the  
3 support, said surface having an increased  
4 tortuosity compared to the tortuosity of the  
5 rest of the support.  
6
- 7 32. A method as claimed in claim 30 or claim 31,  
8 wherein the coating comprises a metal oxide or  
9 metal oxide precursor.  
10
- 11 33. A method as claimed in claim 32, wherein the  
12 metal oxide or precursor comprises a group IV  
13 metal oxide or group IV metal oxide precursor.  
14
- 15 34. A method as claimed in claim 33, wherein the  
16 group IV metal oxide or precursor comprises  
17  $\text{TiO}_2$  or a  $\text{TiO}_2$  precursor.  
18
- 19 35. A method as claimed in claim 30, wherein the  
20 coating produces a flux control layer on the  
21 membrane.  
22
- 23 36. A method as claimed in any one of claims 30 to  
24 34, wherein a second coating, the second  
25 coating being a flux control layer, is also  
26 applied to the support.  
27
- 28 37. A method as claimed in claim 35 or 36, wherein  
29 the flux control layer is applied to the  
30 membrane by exposure to a boemite sol.  
31

- 1 38. A method as claimed in any one of claims 28 to  
2 36 wherein the coating and/or the second  
3 coating is applied by dipping the support into  
4 a liquid comprising the coating.  
5
- 6 39. A method as claimed in any one claims 28 to  
7 38, including the step of applying the  
8 catalyst to a surface of the membrane by  
9 passing a catalyst precursor solution over a  
10 first surface of the support and an osmotic  
11 solution over the opposite surface of the  
12 support, and allowing the catalyst or a  
13 catalyst precursor to be deposited on the  
14 support via the process of osmosis.  
15
- 16 40. A method as claimed in any one of claims 28 to  
17 39, further including the steps of drying the  
18 support and heating/firing the support.  
19



2 / 15

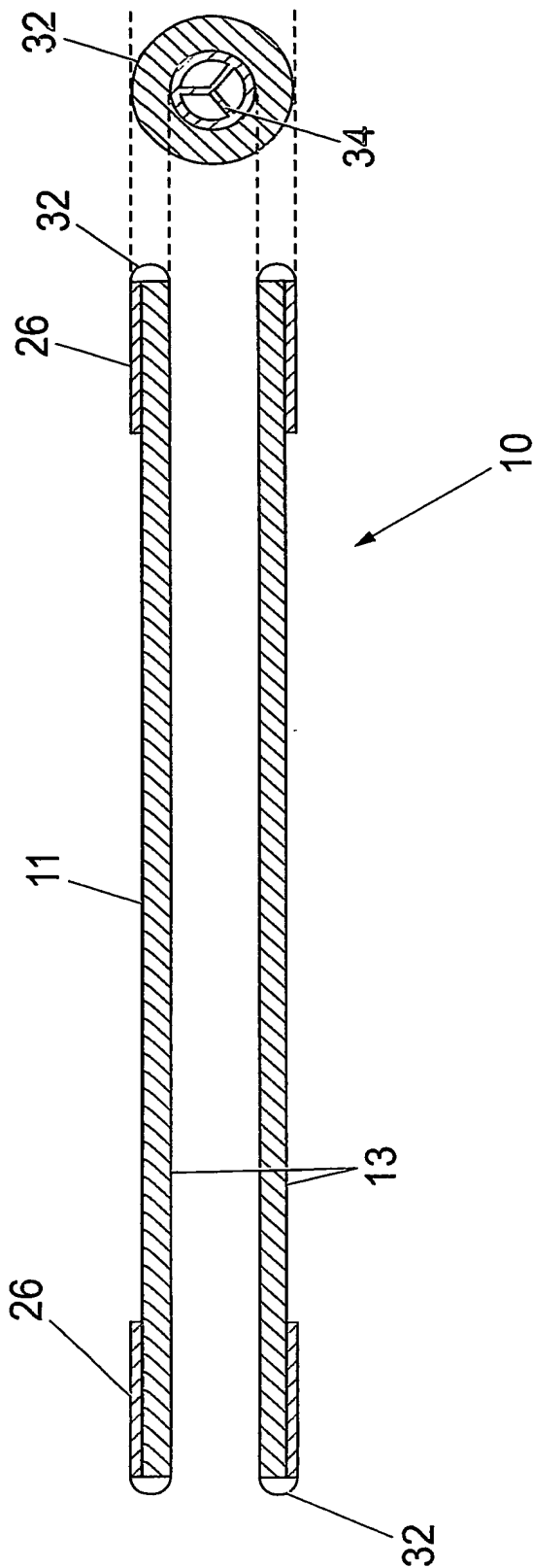
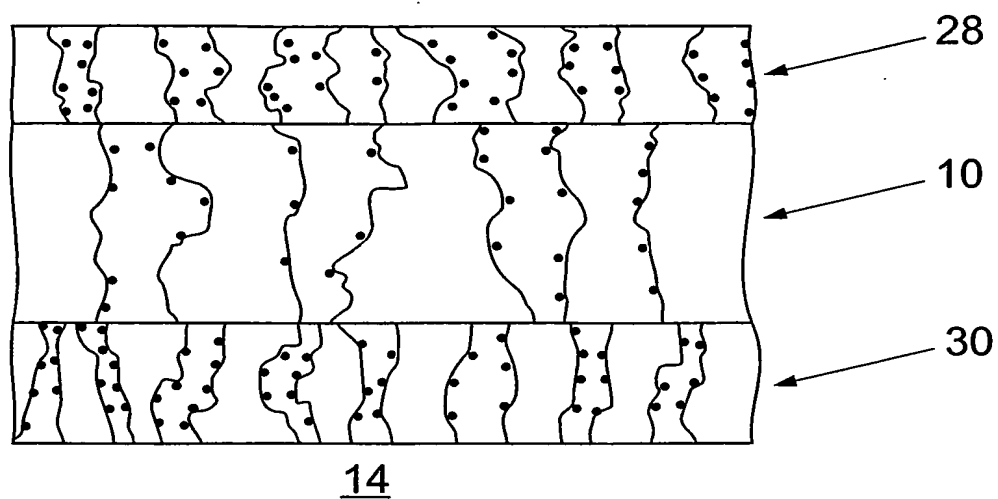


Fig. 2b

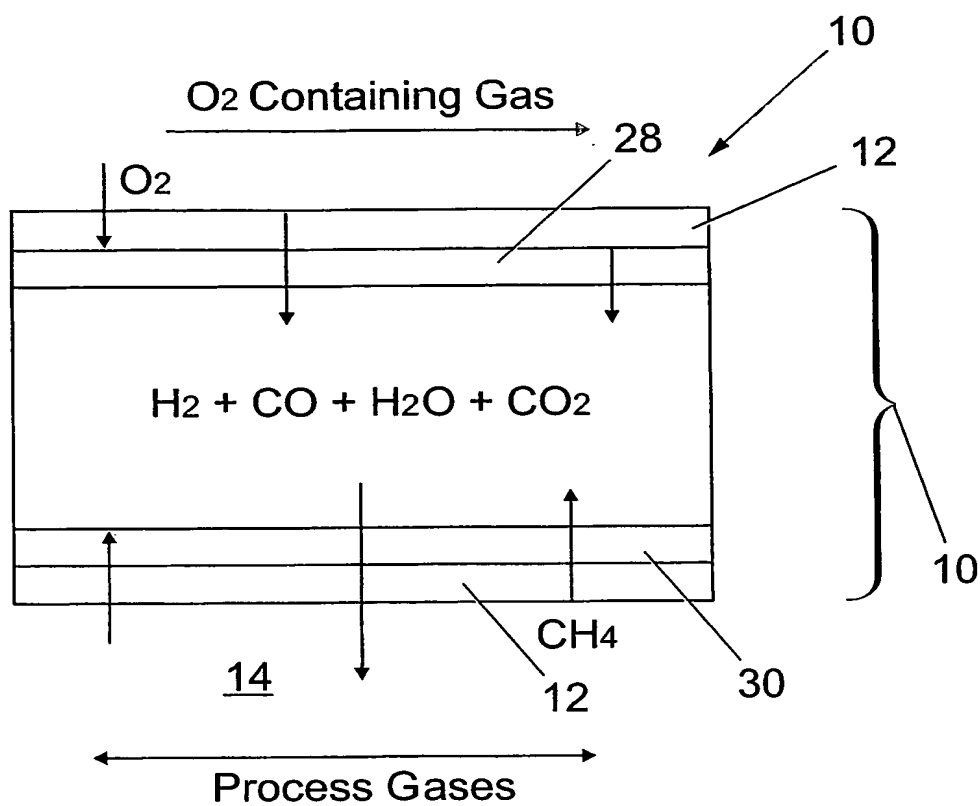
Fig. 2a

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3 / 15

*Fig. 3a*

4 / 15

*Fig. 3b*

20

5 / 15

(CH<sub>4</sub>/O<sub>2</sub> feed = 150/15)

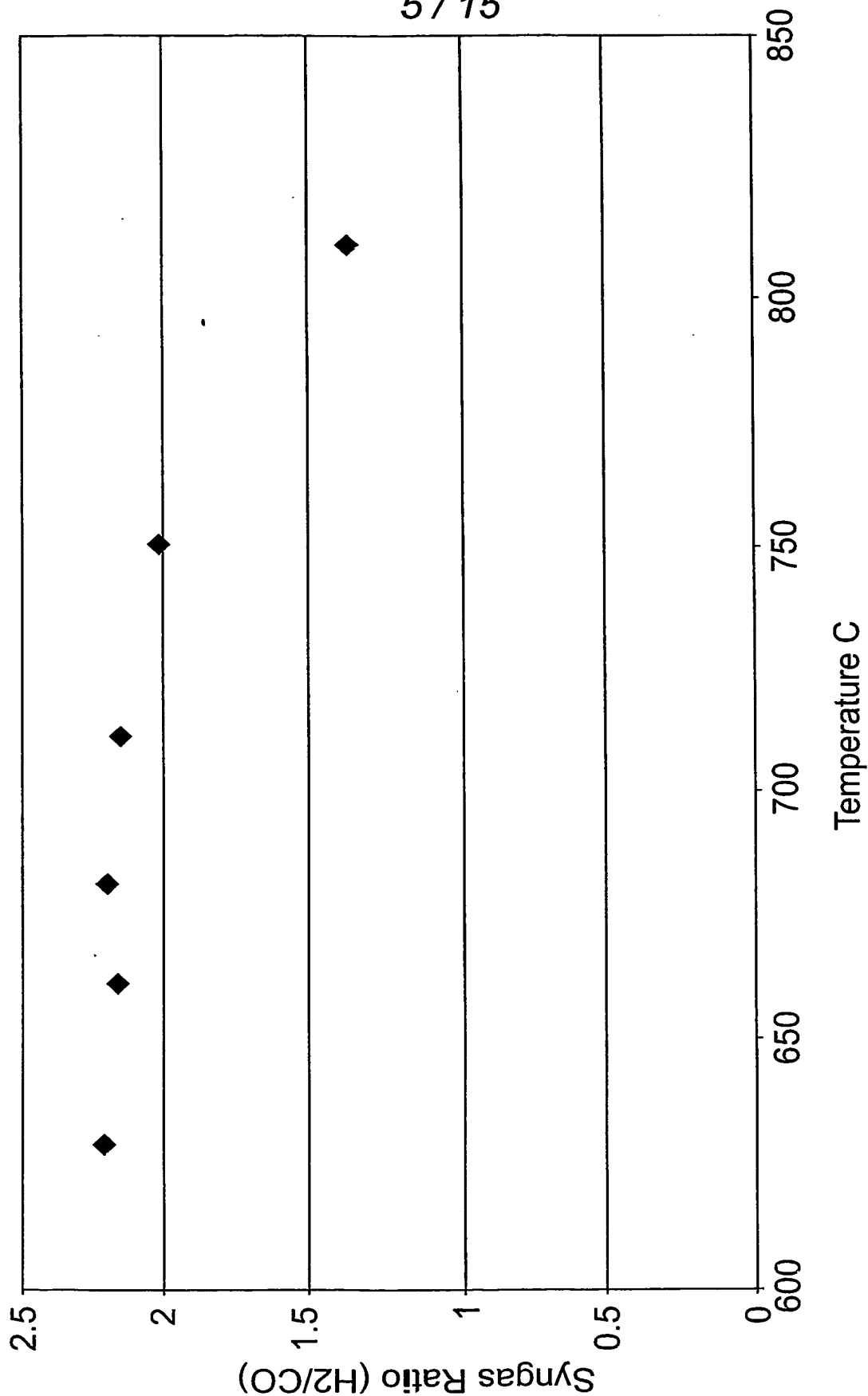
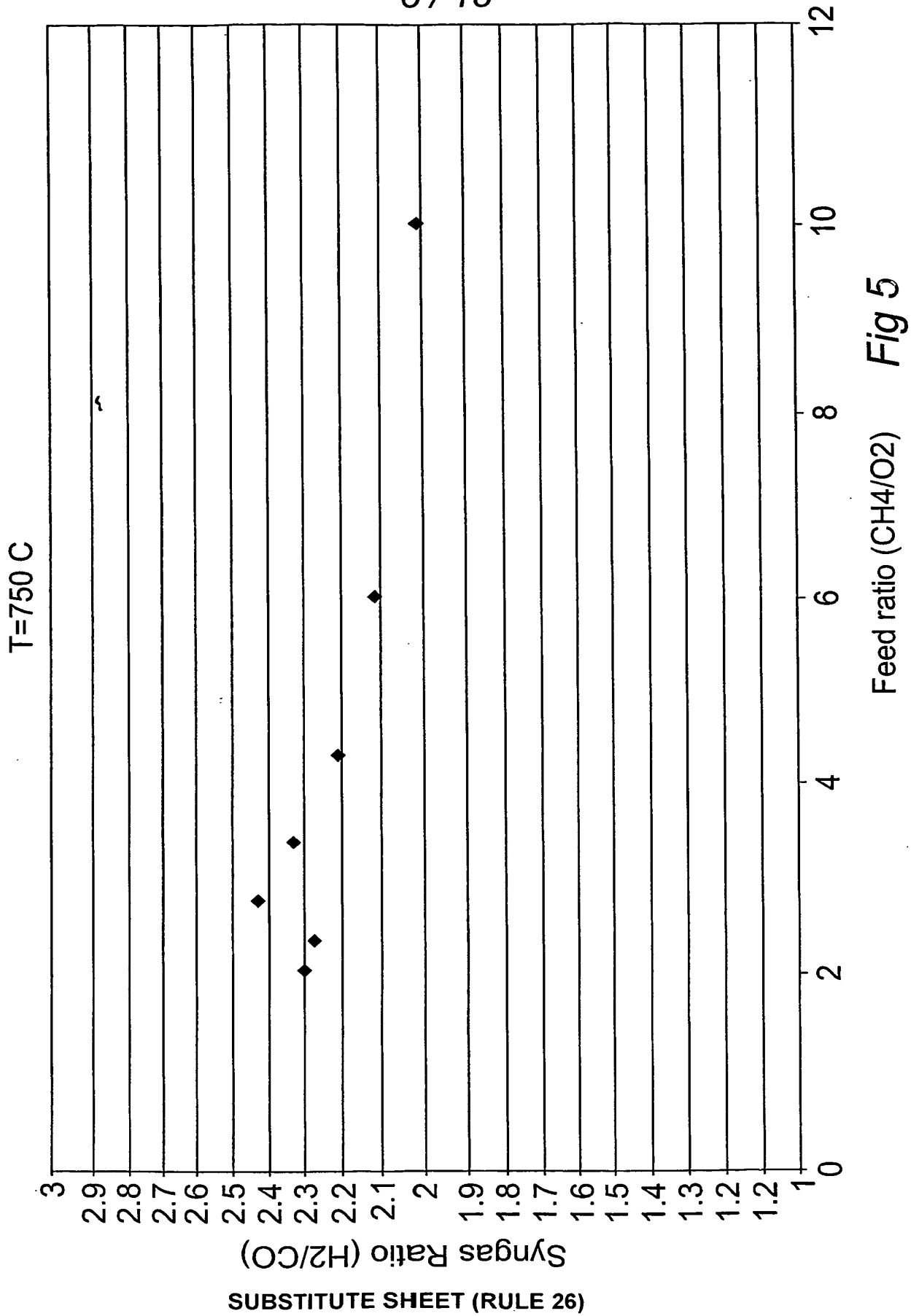


Fig. 4



33

6 / 15



7 / 15

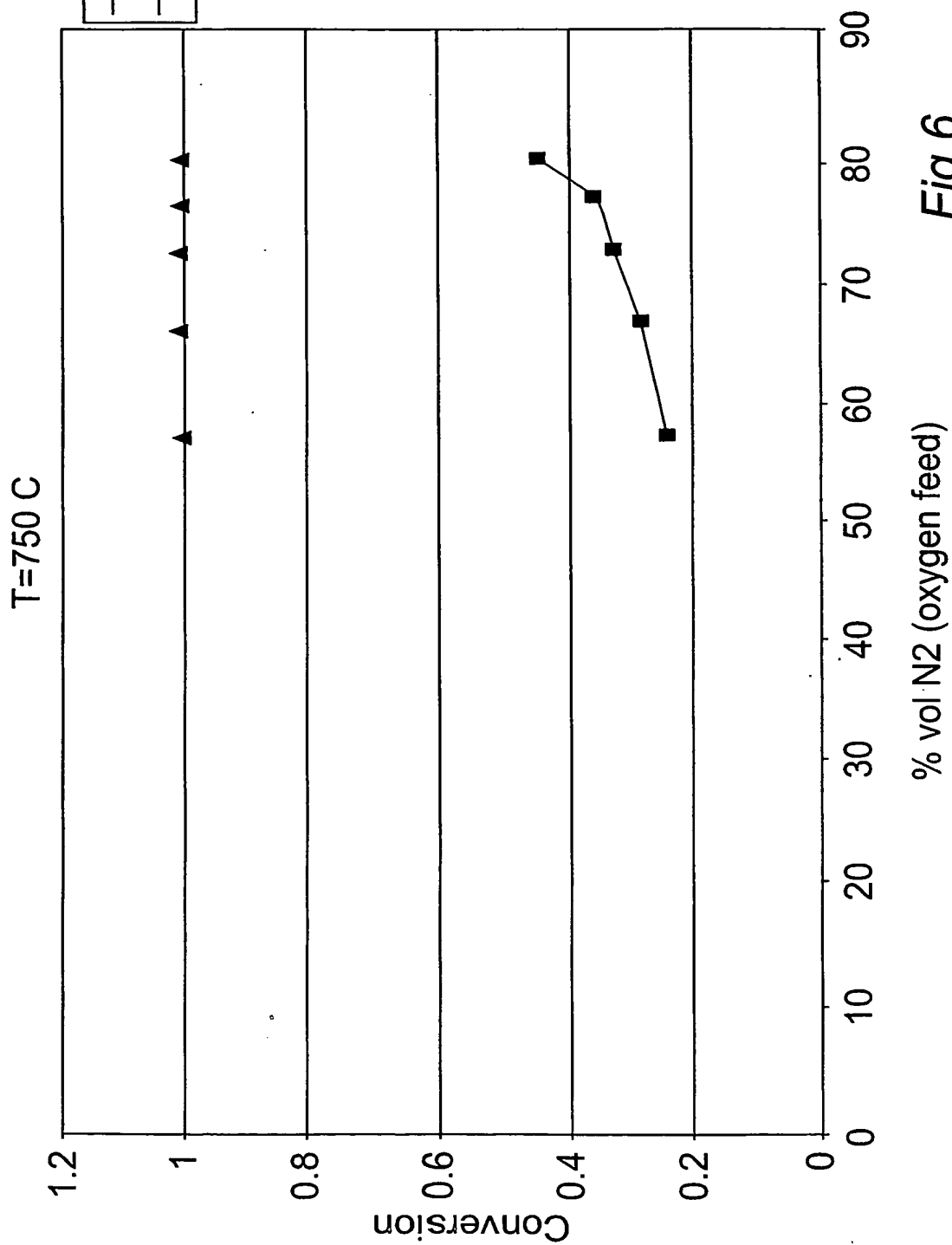


Fig 6

8 / 15

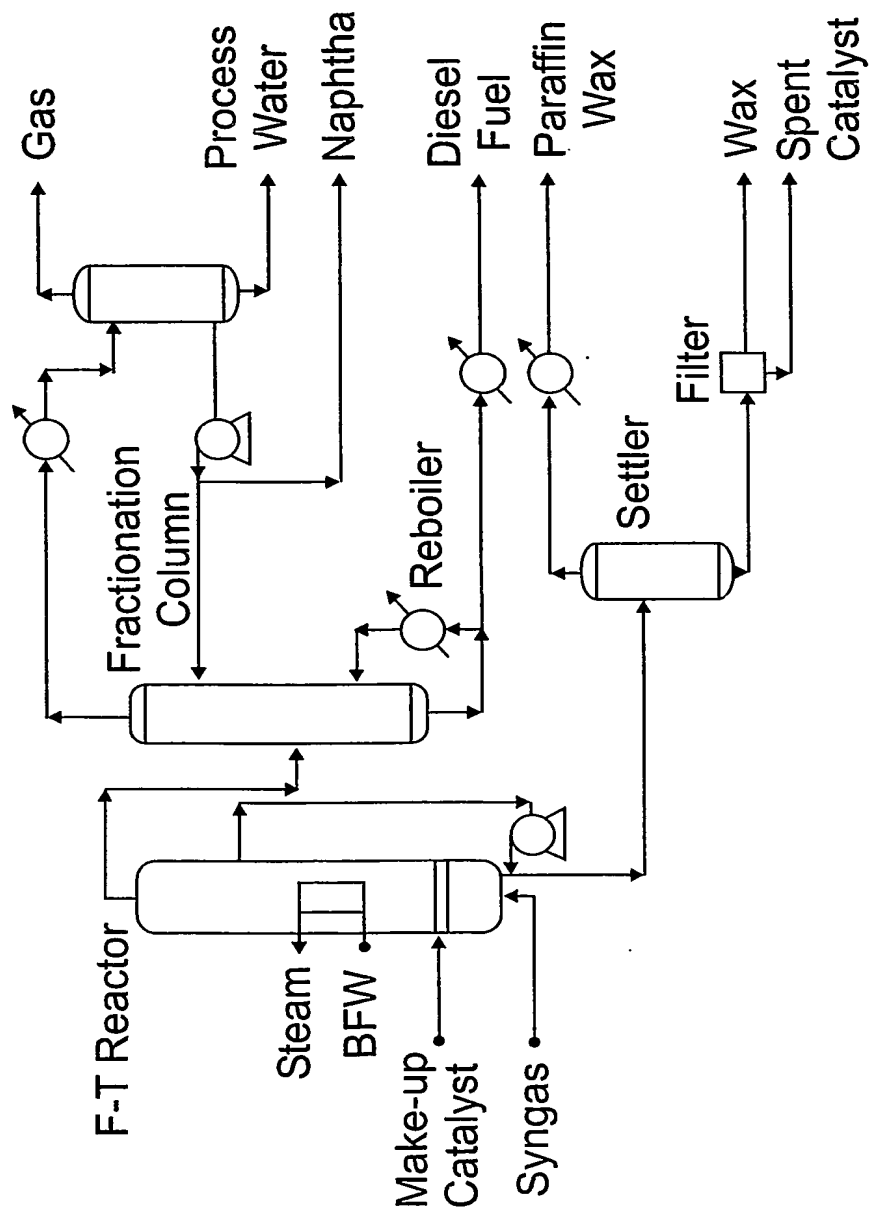


Fig 7

9 / 15

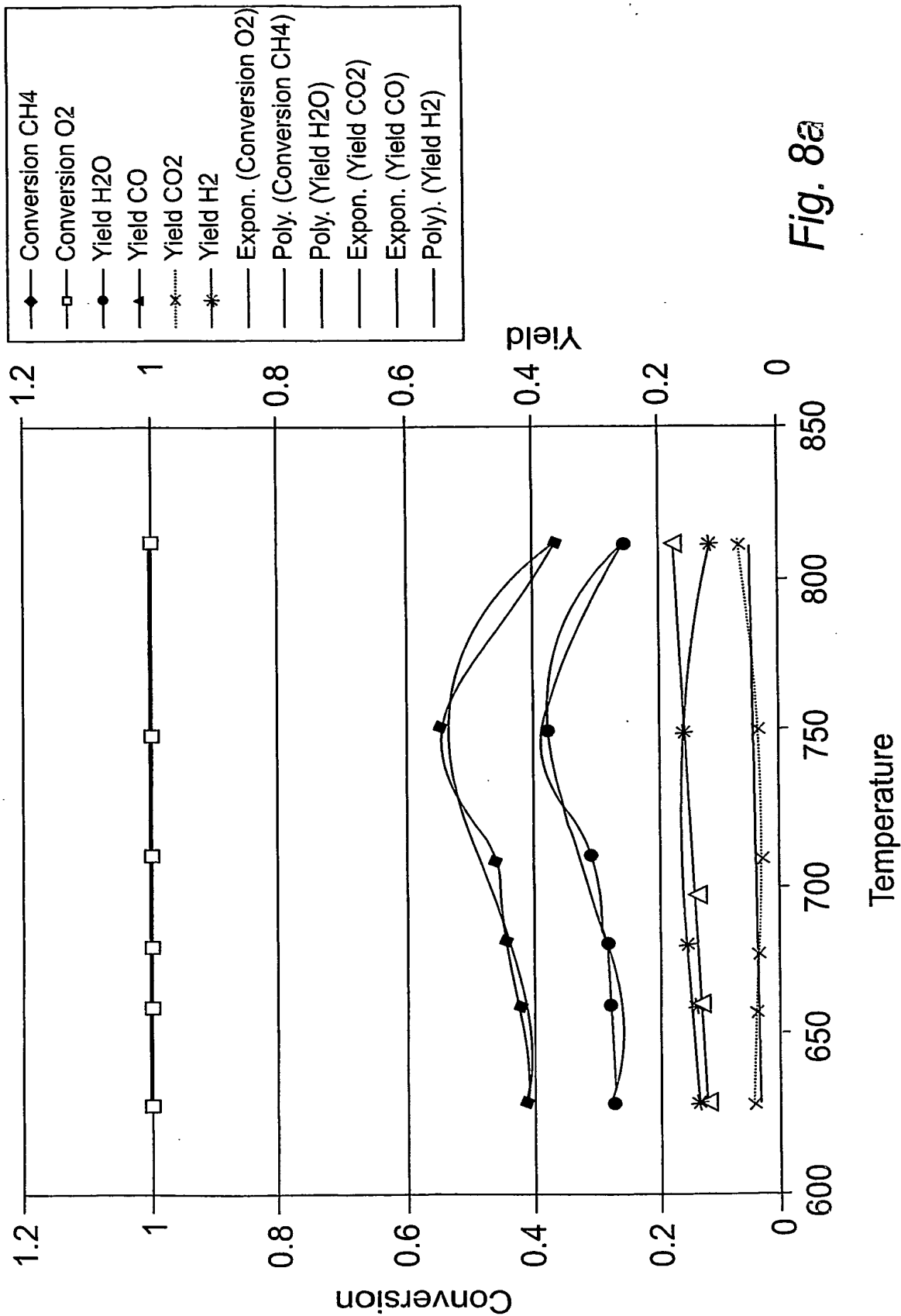
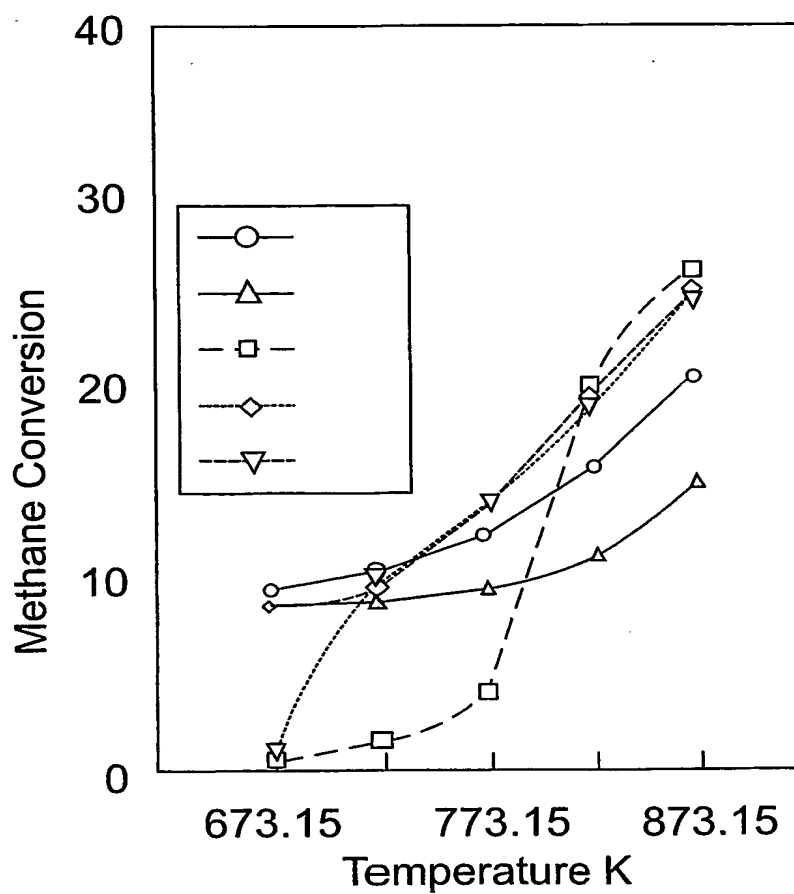


Fig. 8a

20

10 / 15

*Fig 8b*

11 / 15

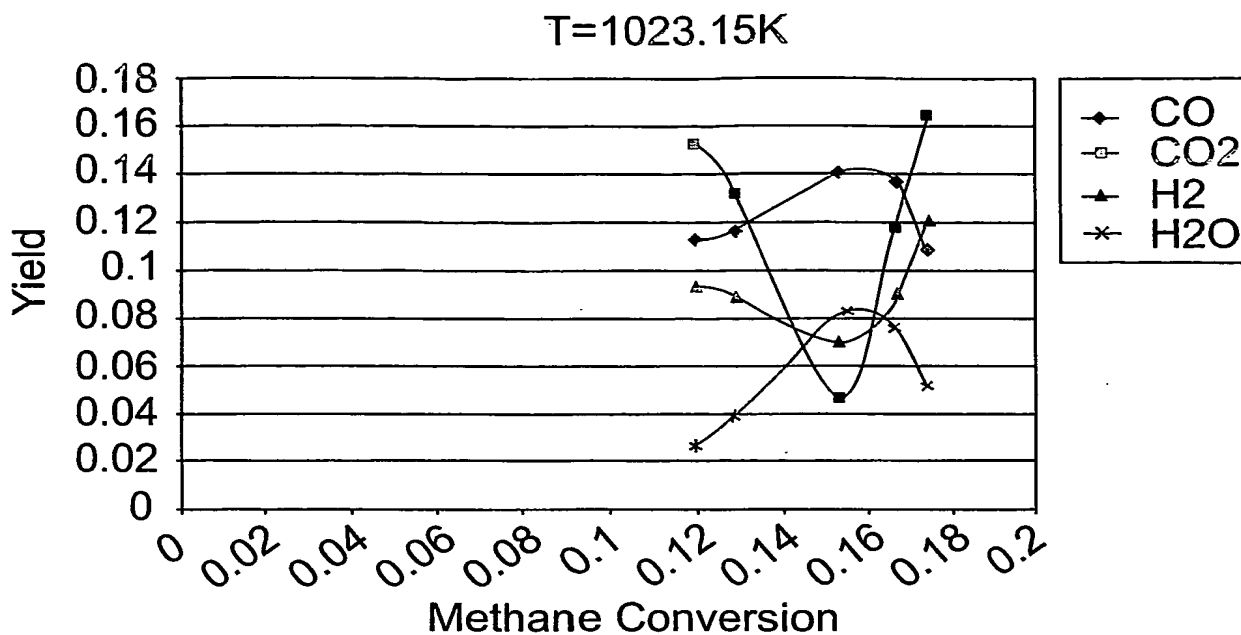


Fig. 9

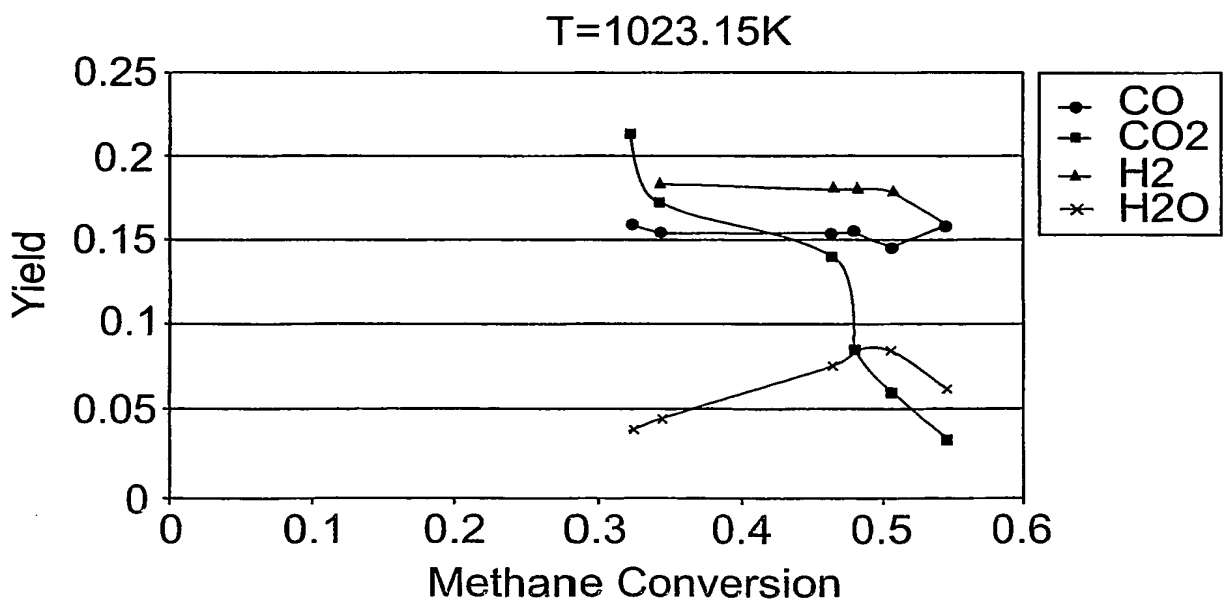


Fig. 10

12 / 15

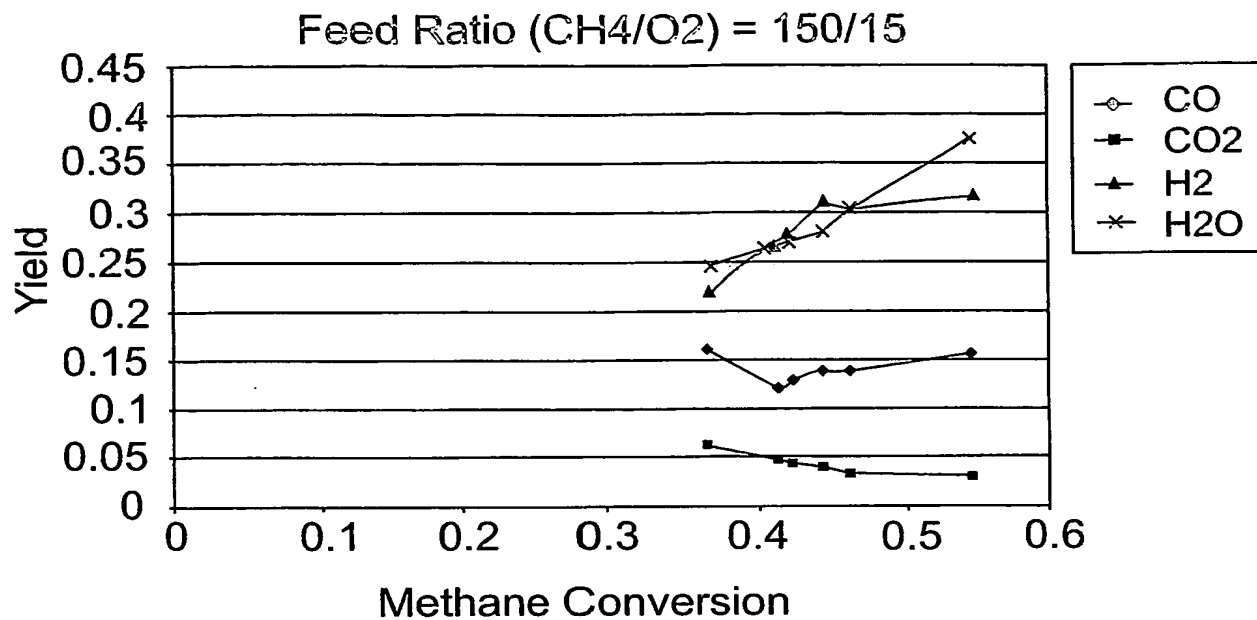


Fig. 11

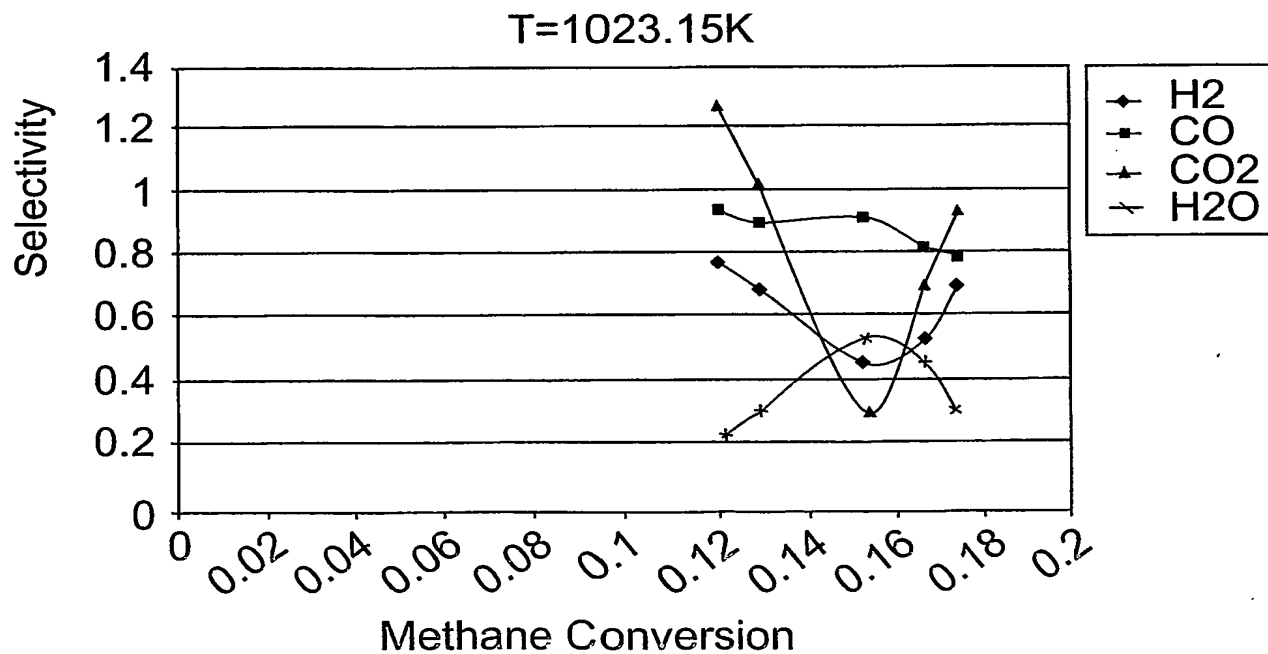
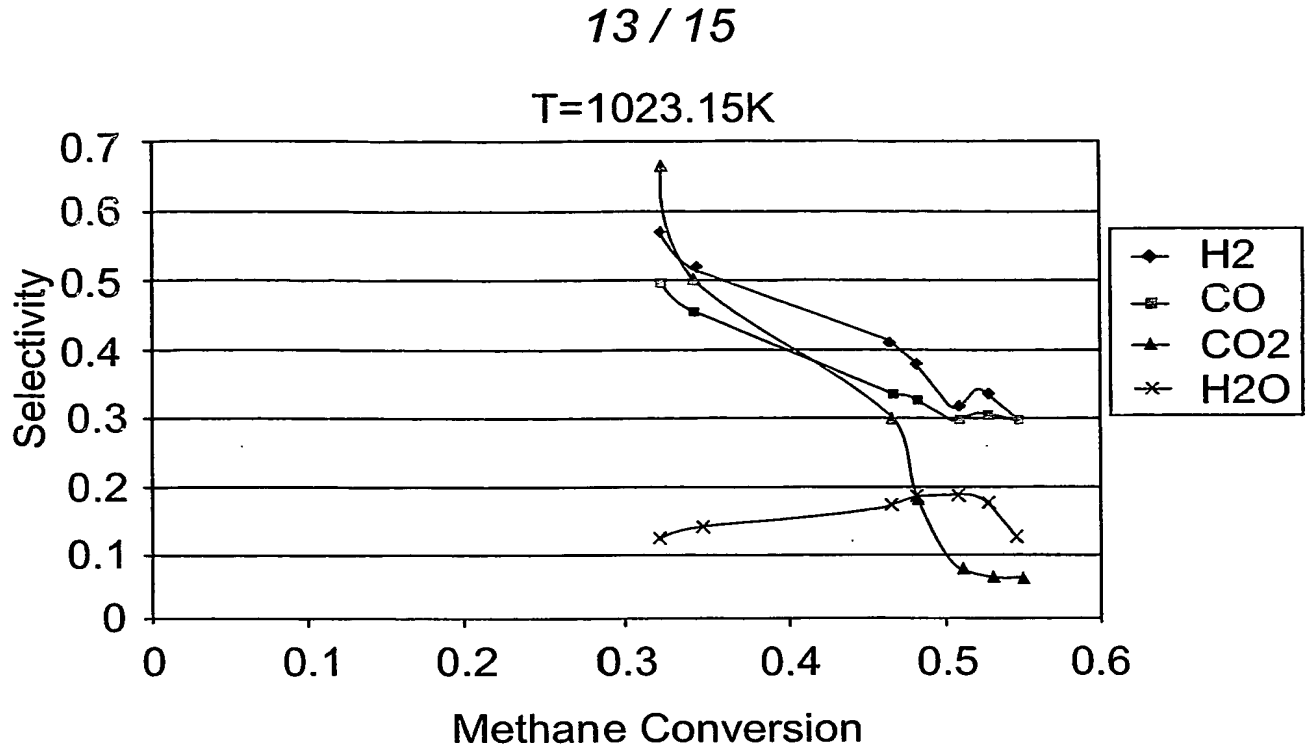
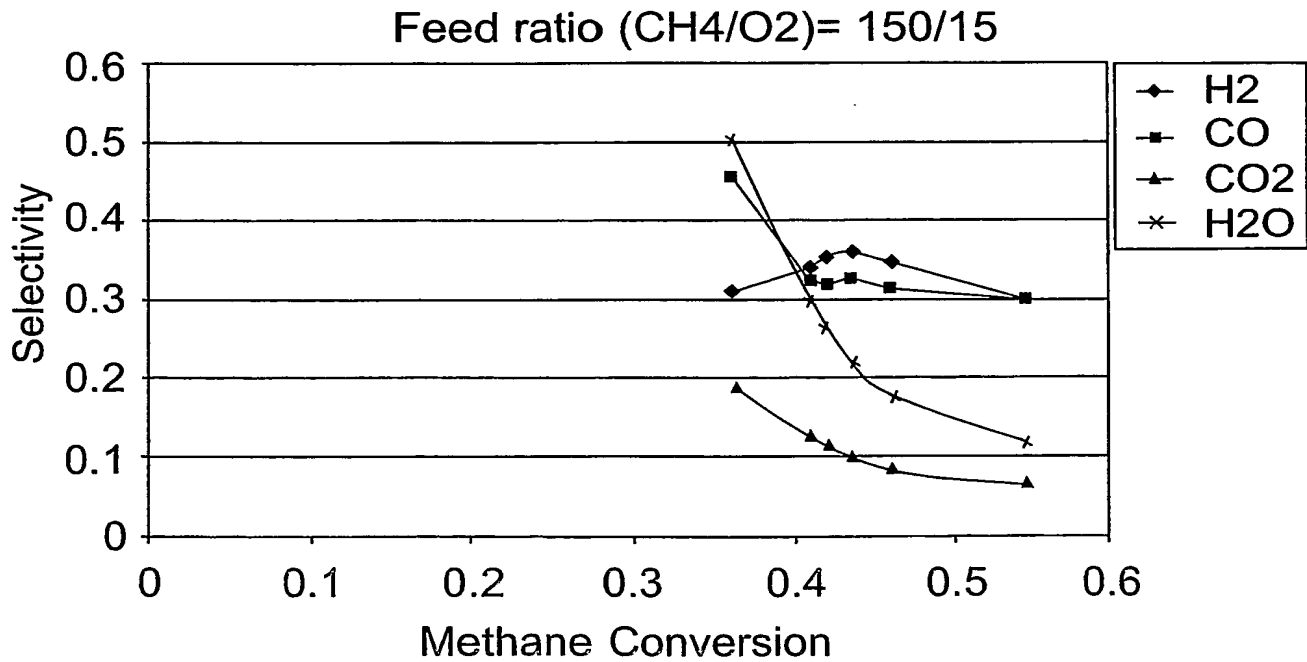


Fig. 12

*Fig. 13**Fig. 14*



14 / 15

T = 1023.15K

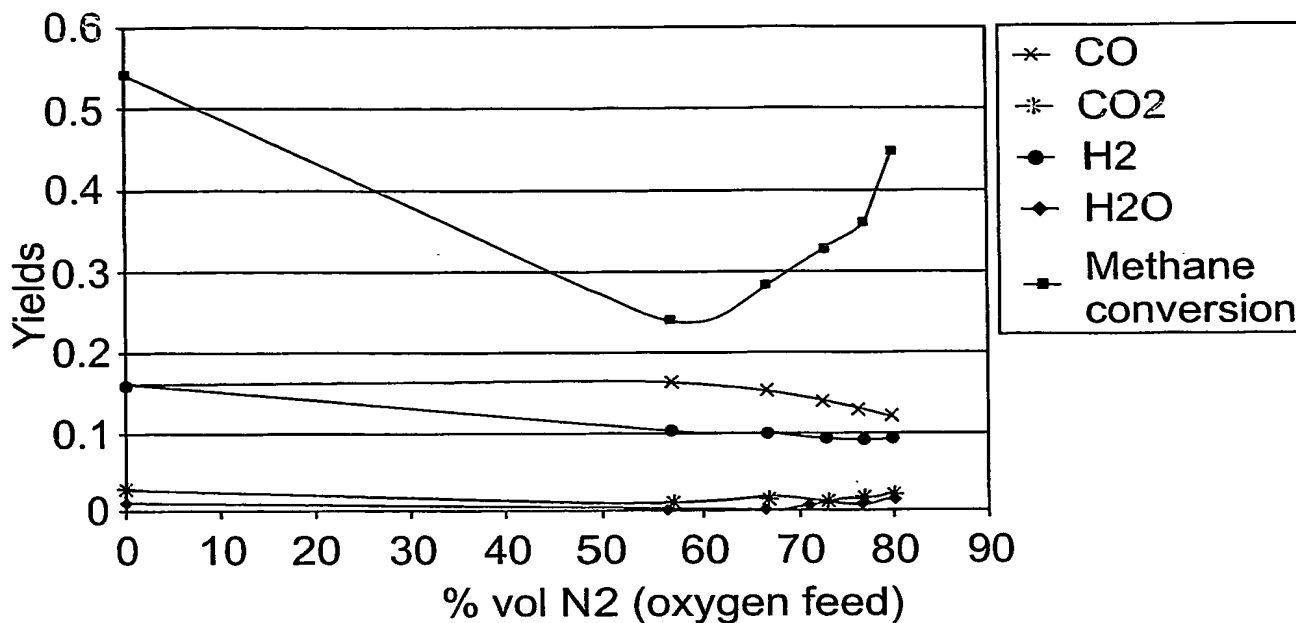


Fig. 15

T = 1023.15K

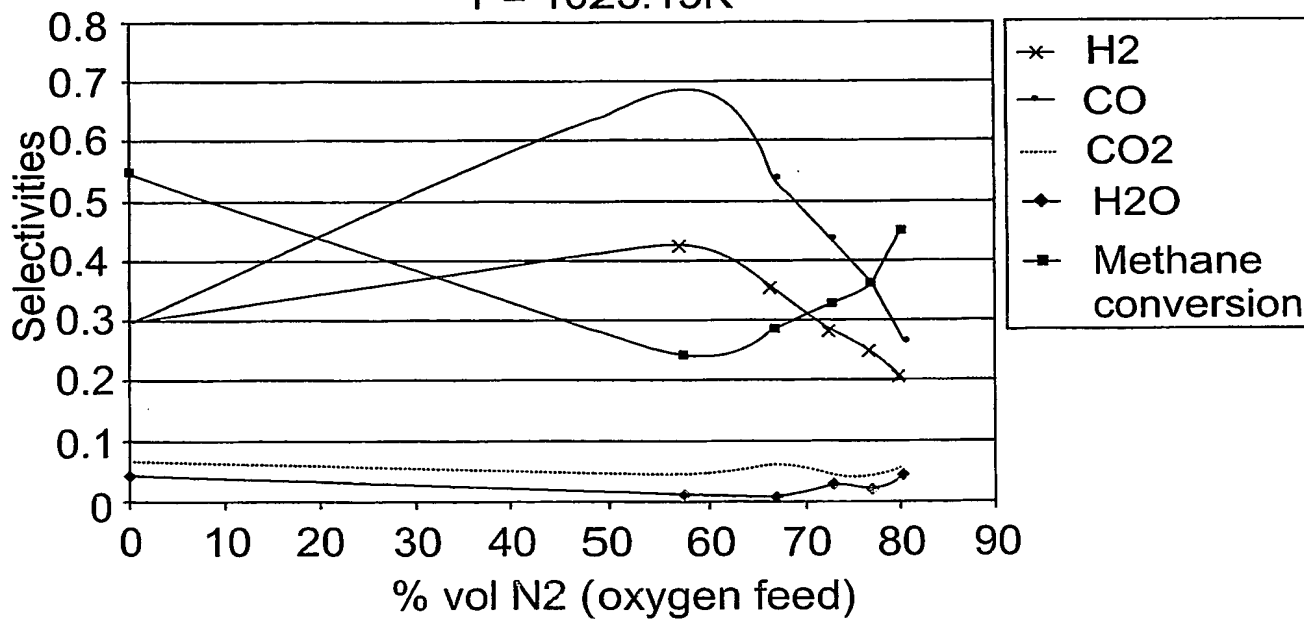


Fig. 16

15 / 15

T = 1023.15K

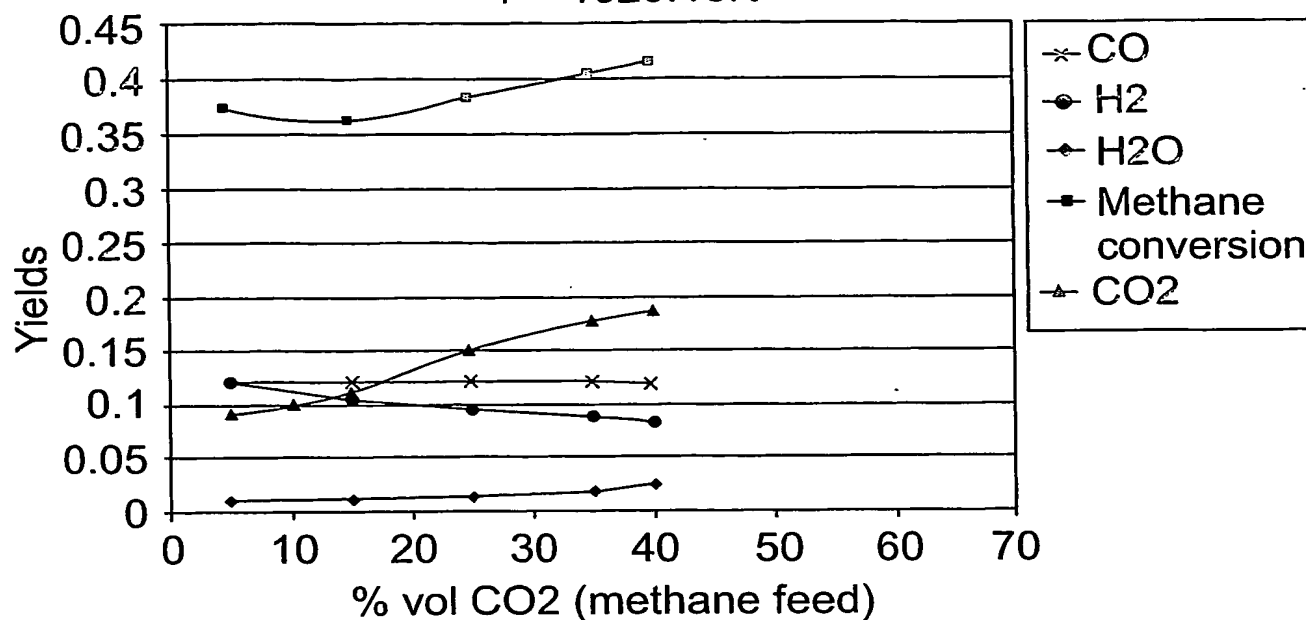


Fig. 17

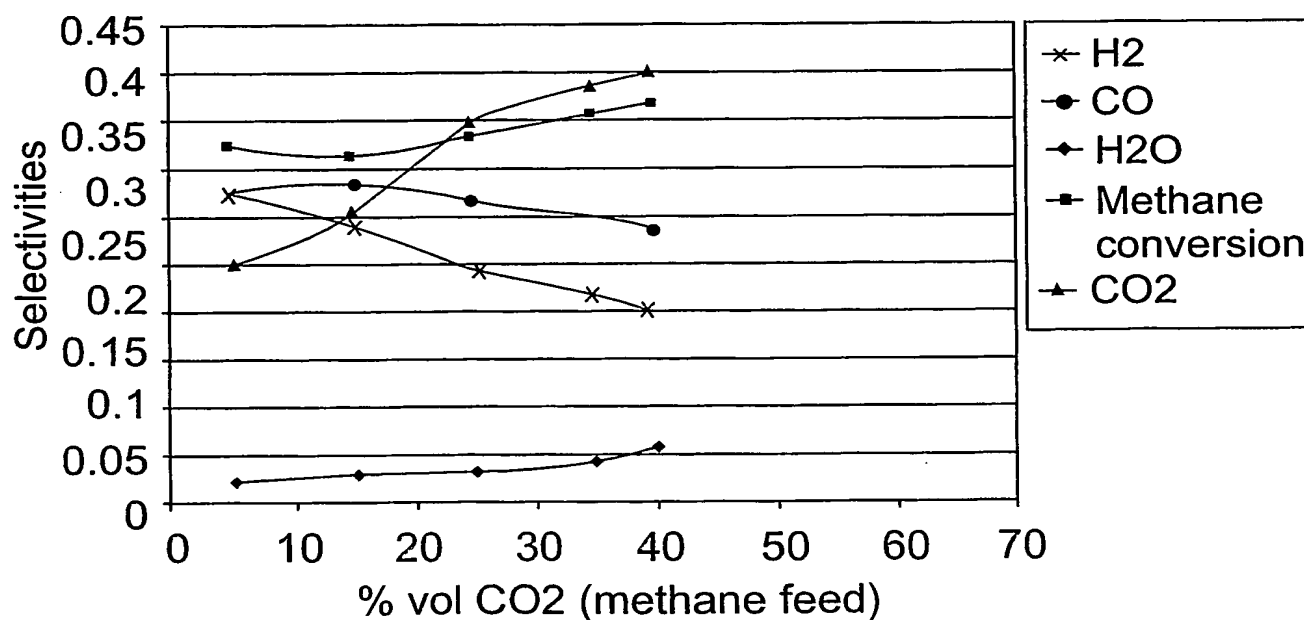


Fig. 18

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB2004/001787

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/22 B01D69/02 C01B3/38 C01B13/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 01/93987 A (PRAXAIR TECHNOLOGY INC) 13 December 2001 (2001-12-13) cited in the application</p> <p>page 3, line 27 - page 4, line 23 page 10, line 19 - page 11, line 24 page 12, lines 1-4 page 13, line 12 - page 17, line 9; figures 1-3</p> <p style="text-align: center;">----- -/--</p>	<p>1-4, 8, 10-14, 17, 19-25, 28, 29</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 September 2004

Date of mailing of the international search report

01/10/2004

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Semino, D

# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 663 232 A (AIR PROD &amp; CHEM) 19 July 1995 (1995-07-19)</p> <p>page 3, lines 6-25,42 page 5, lines 17-52 page 7, line 51 - page 8, line 1; example 8</p>	<p>1-4,8, 12-14, 17, 21-25, 28,29</p>
X	<p>US 5 846 641 A (ZHOU MINYAO ET AL) 8 December 1998 (1998-12-08)</p> <p>column 1, line 57 - column 2, line 19</p>	<p>1-3,14, 17, 21-25, 28,29</p>
X	<p>US 2002/022568 A1 (MACKAY RICHARD ET AL) 21 February 2002 (2002-02-21)</p> <p>paragraphs '0003!, '0004!, '0024!, '0030!, '0035! - '0037!, '0042!, '0046!; example 4</p>	<p>1-3,8, 12-14, 17, 19-26, 28,29</p>
P,X	<p>WO 03/099424 A (STATOIL ASA ; BP CORP NORTH AMERICA INC (US)) 4 December 2003 (2003-12-04)</p> <p>page 1, line 19 - page 2, line 34 page 5, line 4 - page 6, line 10 page 7, line 18 - page 8, line 13; figure 1 page 12, line 27 - page 14, line 23; example</p>	<p>1-3,8, 11-14, 17, 19-25, 28,29</p>
A	<p>US 5 980 840 A (KOBYLINSKI THADDEUS P ET AL) 9 November 1999 (1999-11-09) column 1, line 28 - column 3, line 3 column 6, line 7 - column 7, line 48</p>	<p>1-40</p>

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